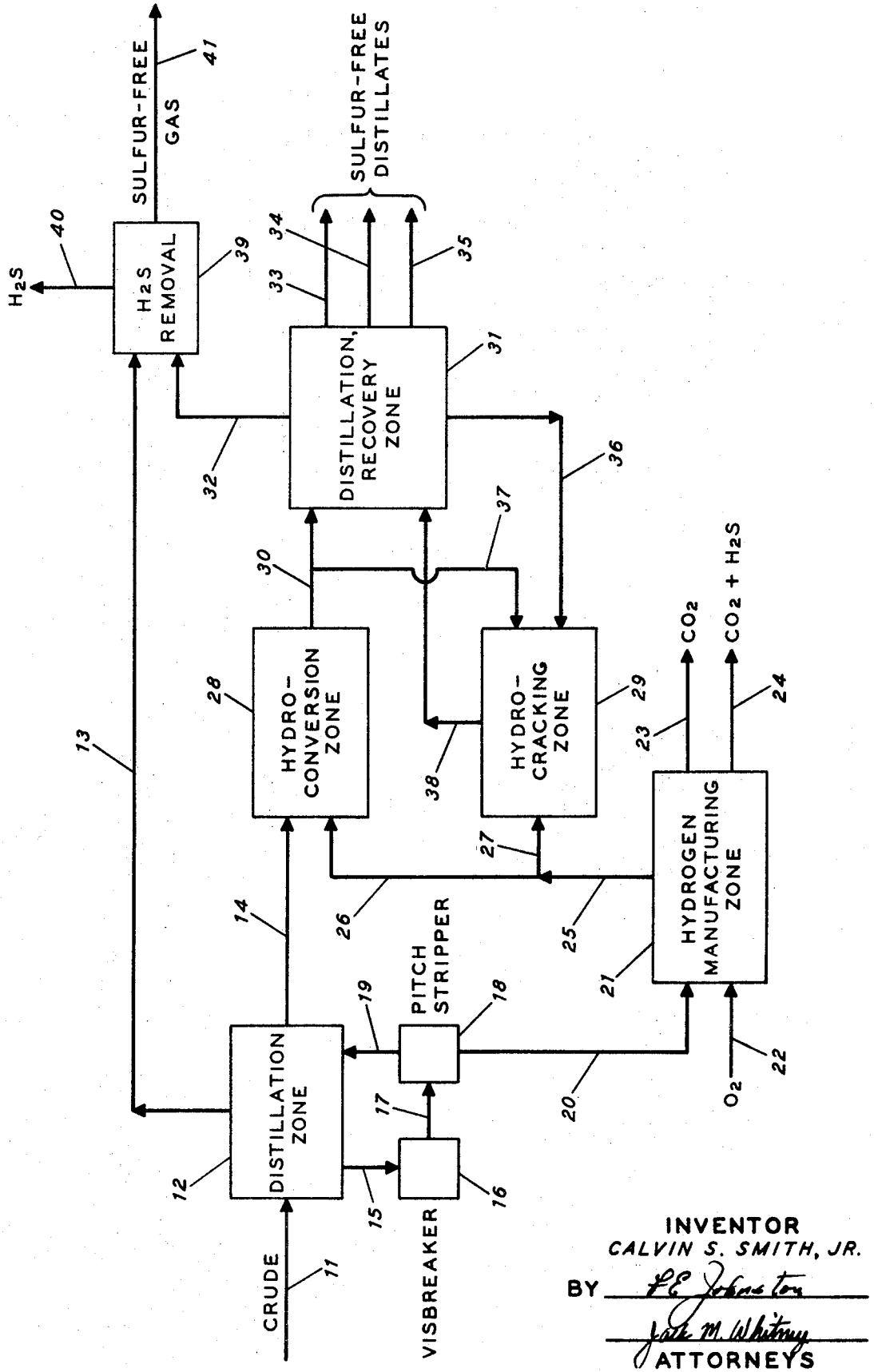
Nov. 3, 1970 C. S. SMITH, JR 3,537,977

REFINERY UTILIZING HYDROGEN PRODUCED FROM A PORTION OF THE FEED

Filed July 8, 1968



INVENTOR
CALVIN S. SMITH, JR.

BY P E Johnston
Jack M. Whitney
ATTORNEYS

United States Patent Office 3,537,977 Patented Nov. 3, 1970

3,537,977

REFINERY UTILIZING HYDROGEN PRODUCED FROM A PORTION OF THE FEED

Calvin S. Smith, Jr., El Cerrito, Calif., assignor to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

Continuation-in-part of application Ser. No. 601,486, Dec. 13, 1966. This application July 8, 1968, Ser. No. 747,419

Int. Cl. C10g 23/00

U.S. Cl. 208—89 5 Claims

ABSTRACT OF THE DISCLOSURE

A high yield all-hydrocracking overall refinery process for converting sulfur-containing crude oil to substantially sulfur-free distillate products wherein, for example, partial oxidation of a stripped visbreaker tar is used to provide the hydrogen requirements for a two-stage hydrocracker treating all of the crude distillates and essentially the only products are sulfur-free distillates and light products with essentially no production of sulfur-containing residuals such as coke or fuel oil.

CROSS REFERENCES

This application is a continuation-in-part of my application Ser. No. 601,486, filed Dec. 13, 1966, and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to the refining of crude petroleum and like hydrocarbonaceous materials of ancient origin. More particularly, the invention relates to hydrocarbon oil refining processes wherein at least a portion of the hydrocarbon oil is upgraded by treating with hydrogen.

Discussion of the present invention in relation to the prior art

The historical development of the petroleum refining industry has been characterized by a steadily increasing demand for lower boiling, higher quality, distillate products, and decreasing demand for the higher boiling heavy fuel oil components of the crude. In recent years this has been aggravated by restrictions being placed on the burning of sulfur-containing fuel oils which produce noxious atmospheric-polluting gases. Consequently, in some areas heavy fuel oil is no longer a salable product; and the desirability of converting the crude oil entirely to sulfur-free products becomes apparent.

For reducing the yield from crude of high boiling sulfur-containing heavy fuel oil, various combinations of treating processes have been devised, including atmospheric and vacuum distillation of the crude, catalytic cracking of the highest boiling distillate portions, thermal cracking and coking of high boiling distillate and residual portions, and hydrofining, hydrocracking, and reforming of the lighter distillate fractions produced by these various treatments. The amount of leftover residue can be reduced to a small amount by combinations of these techniques, particularly if coking is applied to the highest boiling residual fraction. In that case, however, there is produced a sulfur-containing coke product which cannot always be disposed of and which is similarly subject to the restrictions against burning sulfur-containing fuels.

In accordance with the present invention, it is proposed to separate the crude oil into two principal fractions: a first fraction which is converted to carbon dioxide and hydrogen, and a second fraction which is treated with the hydrogen so produced for hydrodesulfurization and hydrocracking to produce upgraded distillates. It is proposed that the first fraction comprise the highest boiling portion of the crude oil and the second fraction comprise the lower boiling portion, which is more amenable to hydrodesulfurization and hydrocracking than the crude residue. Thus the invention contemplates upgrading the distillate portions of crude by hydrogen-consuming reactions and using the nondistillable residue as the raw material for manufacturing the hydrogen to be consumed. The crude residue can be converted essentially quantitatively to carbon dioxide and hydrogen in a known manner, by reacting the residual fraction with molecular oxygen at partial oxidation conditions for synthesis gas generation in a hydrogen-manufacturing zone, shift converting carbon monoxide in the combusted gas mixture of carbon monoxide and hydrogen thereby produced to form carbon dioxide and additional hydrogen, and removing the carbon dioxide, along with hydrogen sulfide produced from the sulfur in the crude residue, to provide high purity hydrogen.

With heavy sulfur-containing crude oils, the usual situation heretofore has been that the high boiling portion or residue, remaining even after vacuum distillation of the crude, is more than is needed to manufacture sufficient hydrogen for upgrading of the distillate portions, because the refinery schemes have included coking or catalytic or thermal cracking of a portion of the highest boiling distillates and/or the recovery of substantial amounts of straight-run distillates and/or upgrading of fractions by solvent treatments or like processes not requiring the use of hydrogen. Hydrogen used in hydrofining the gasoline produced could be adequately supplied by catalytic reforming. Additional hydrogen was needed only to desulfurize the cycle oils and straight-run furnace and diesel oils.

In contrast, the present invention contemplates upgrading essentially the entire distillate portion of crude oil entirely by hydrogenation and hydrocracking, to the substantial exclusion of alternate upgrading techniques which might otherwise have been selected, thus providing an all-hydrocracking refinery.

It has been found that the all-hydrocracking concept of the present invention gives surprisingly economic superiority over traditional overall refinery processing arrangements. Contrary to previous expectations, upon analysis it was found that the all-hydrocracking overall refinery process in accordance with the present invention is notably superior to, for example, perhaps the currently most widely used overall refinery process arrangement which includes a catalytic cracking unit, the most preferable generally being a Fluid Catalytic Cracking unit (FCC). The all-hydrocracking refinery process of the present invention is particularly advantageous when there is low demand for fuel oil and high demand for jet fuel and motor gasoline. In the comparison summarized by Tables I through III below, a generally favorable FCC-hydrocracking process arrangement is compared to the all-hydrocracking process arrangement. For fairness of comparison, the two refineries were designed to produce products which are very nearly identical; Table I shows the calculated products from each refinery as well as the feed. Table II gives a breakdown of the capital investment required for each refinery. The grand total at the bottom of Table II shows the all-hydrocracking refinery costs less to build than the FCC-hydrocracking refinery producing the same amount of importatnt major products. Lastly, Table III summarizes the overall economic comparison. From Table II it is seen that the all-hydrocracking refinery requires less investment than the FCC-hydrocracking refinery, but yet the all-hydrocracking refinery has an income advantage of $6,000,000/year in reduced raw material and operating costs. In addition, the

all-hydrocracking refinery has the capability (flexibility) of producing 10,000 b.p.c.d. more jet fuel than the FCC-hydrocracking refinery as the latter is more restricted to the production of automobile gasoline. The flexibility of the all-hydrocracking refinery to produce more jet fuel is important in view of the rapidly increasing jet fuel market.

TABLE I.—STOCK BALANCE COMPARISON

	FCC-hydrocracking, BPCD	"All hydrocracking," BPCD
Input:		
Composite California crude	154,910	147,774
Natural gaso. and misc	17,964	17,964
Products:		
Gas as equivalent fuel oil	6,449	4,549
Propane	4,413	4,993
iC_4	0	883
nC_4	3,161	0
Mogas	98,120	98,120
JP-4 jet fuel	4,081	4,081
Jet fuel A-1	30,930	30,930
Solvents	1,426	1,426
Diesel, auto	2,440	2,440
Stove oil	200	200
Diesel, furnace	12,450	12,450
Asphalt	2,660	2,660
Fuel oil	3,100	0
Sulfur	(1)	(2)
Ammonia	(3)	(4)

1 350 ton. 2 355 ton. 3 50 ton. 4 51 ton.

TABLE II.—CAPITAL INVESTMENT COMPARISON

	FCC and hydrocracking		"All hydrocracking"	
	Capacity—B/CD	Dollars (million)	Capacity—B/CD	Dollars (million)
On Plot:				
Crude unit	154,900	16.9	147,774	15.8
Solvent plant		1.0		1.0
FCC	42,500	15.3		
Resid. hydrocracker	38,200	13.1	33,400	12.1
Isomax	52,600	31.2	70,000	40.0
Hydrofining	31,200	5.3	31,200	5.3
Cat. ref.:				
1st stage	20,200	3.2	15,600	2.7
2nd stage	40,300	8.6	46,200	9.4
C_3–C_4 alkylation	5,600	6.5		
C_5–C_6 alkylation	11,100	6.2	18,600	9.0
Part. oxid., M SCFD	182	32.0	219	36.5
NH_3–H_2S separation, lb./hr.	210,000	3.0	210,000	3.0
Sulfur, T/day	350	1.7	350	1.7
Process plts. total		144.0		136.5
Utilities:				
Steam, lb./hr	650,000	5.5	500,000	4.0
Water treating, lb./hr	1,000,000	3.0	1,000,000	3.0
Water supply		.6		.6
Drains and waste disposal		2.0		2.0
C.W., g.p.m.	167,000	4.4	178,000	4.6
Relief, fuel gas, fuel oil		1.0		1.0
Elect. power, kw	101,000	5.3	113,000	5.9
Tanks and Lines, Etc.:				
Tanks and lines	(1)	31.5	(2)	30.0
NH_3		.4		.4
Propane		.5		.5
Loading racks, bbl. filling and solvent storage		2.5		2.5
Other:				
Marine		5.0		5.0
Bldgs.		5.0		5.0
Site development		5.5		5.5
Land		10.0		10.0
Nonprocess total		77.2		75.0
Overhead		2.5		2.5
Grand total		223.7		214.0

1 9.3 M bbl. 2 8.8 M bbl.

TABLE III.—OVERALL ECONOMIC COMPARISON

	FCC-hydrocracking	"All hydrocracking," per day
Savings on raw materials (primarily crude feed)	*0	+$20,400
Incremental profit on by-products	0	−$10,400
Savings on operating costs	0	+$6,600
Total	0	$16,600

* Base.

Net income advantage of "All Hydrocracking" vs. FCC-Hydrocracking at 95% yearly operating factor .95×365×$11,000/day=$6,000,000/yr.

Capital investment savings for "All Hydrocracking" vs. FCC-Hydrocracking. See Table I, 223.7−214.0=$9,700,000.

THE INVENTION

The present invention provides a process for converting sulfur-containing crude oil substantially entirely to sulfur-free distillate products and gaseous by-products. In accordance with the invention, the crude oil is first separated into essentially three fractions: a normally gaseous fraction, a sulfur-containing distillate fraction, and a sulfur-containing residual fraction. The residual fraction is reacted with molecular oxygen at partial oxidation conditions for synthesis gas generation in a hydrogen manufacturing zone, the carbon monoxide produced is shift converted to carbon dioxide, and the carbon dioxide and hydrogen sulfide are removed to provide high purity hydrogen. The entire sulfur-containing distillate fraction is reacted with a portion of the said high purity hydrogen in contact with a sulfactive hydrogenation catalyst at elevated temperature and pressure in a hydroconversion zone, whereby sulfur compounds in the distillate are converted to H_2S and there are formed gaseous by-products and hydrofined distillate. At least a portion of the hydrofined distillate is reacted with the remaining portion of the high purity hydrogen in contact with an active hydrocracking catalyst at elevated temperature and pressure in another hydroconversion zone, thereby converting hydrofined distillate to hydrocracked lower boiling distillate and forming gaseous by-products. Hydrogen sulfide is removed from the treated distillate and by-products to recover gaseous by-products and to recover sulfur-free distillate products comprising the hydrocracked distillate and any hydrofined distillate which was not hydrocracked. The amount of hydrofined distillate which is hydrocracked, and the extent of conversion, are such that all the hydrogen produced from the residual fraction is consumed in hydroconversion.

The present invention thus provides for balancing the hydrogen consumed in the hydrofining and hydrocracking processes with the hydrogen produced by the partial oxidation of the residue. In the case of heavy crude oils, it

is often desirable to reduce the quantity of heavy residue remaining to less than a vacuum residuum, because the hydrogen required for satisfactory upgrading of the distillate portion may be less than can be produced from a vacuum residue. In one preferred embodiment of the invention, the crude oil is separated into the three fractions by a combination of distilling the crude oil under vacuum, visbreaking the vacuum distillation bottoms, and stripping gaseous by-products and additional sulfur-containing distillate from the visbreaker effluent in a pitch stripper, forming the sulfur-containing residual fraction as the pitch stripper bottoms which feeds the hydrogen plant. In a second embodiment, the vacuum residuum is processed through a solvent deasphalting unit, and the bottoms from the solvent deasphalter used to make hydrogen. In a third embodiment, the vacuum residuum is processed through resid hydrocracking and the bottoms from this unit used to make hydrogen. In such case, fuel oil production is low or zero; and the necessary hydrogen is produced from the lowest value hydrocarbon.

While, as noted, in the practice of the invention the use of supplementary distillate conversion and upgrading processes not requiring hydrogen is minimized, it is generally desirable to upgrade the octane number of gasoline boiling range distillate products of the process by catalytic reforming of a portion of the sulfur-free distillate produced. In such case, hydrogen produced in the catalytic reforming can be used to augment the supply of high-purity hydrogen produced by the partial oxidation of the residual fraction.

Where, as contemplated in the invention, the distillate upgrading processes involve essentially only hydrogen-consuming hydrofining and hydrocracking reactions, there can be provided an integrated refinery scheme wherein the net input of energy is minimized. The hydrofining and hydrocracking reactions are strongly exothermic, and thus provide a source of high temperature heat energy. This heat energy can be translated into work energy and used to supply a major portion of the work energy required in the hydrogen manufacturing zone. In particular, a major cost factor in the production of hydrogen by partial oxidation of residua is the large amount of energy required to remove the carbon dioxide from the synthesis gas and the energy required for providing the hydrogen at the elevated pressures used in the hydrofining and hydrocracking reactions. The partial oxidation process centers the main power load of the refinery in the air compressors for the oxygen plant, oxygen compression, and hydrogen recycle. All of these loads can be served by centrifugal compressors amenable to steam-turbine drives, and by-product steam generated in removing the exothermic reaction heat of the hydrofining and hydrocracking reactions can be used in automatic extraction condensing steam turbines.

Moreover, the partial oxidation, shift conversion, and hydrogen purification can be carried out at substantially higher pressures than can be used in other hydrogen manufacturing processes such as steam-natural gas reforming. The adverse effect of pressure on the equilibrium reaction $CH_4+H_2O \rightarrow CO+3H_2$, does no enter into consideration at the conditions for partial oxidation of heavy oils, even though steam may be present, because the extent of conversion is primarily determined by reaction kinetics. Thus, partial oxidation is being carried out at 600 p.s.i.; operations at 1200 p.s.i. have been reported; and it is apparent that even higher pressures of 2000 p.s.i. or more can be used corresponding to the pressure levels used in the hydroconversion reactions. At such pressures the unit costs of gas compression and hydrogen purification are greatly reduced, and energy interchange with the hydroconversion portion of the refinery is facilitated.

It is accordingly part of the concept of the present invention in its preferred embodiments, that the partial oxidation hydrogen manufacturing is to be carried out at a high pressure above 600 p.s.i.g.. Specifically, the pressure should be at least 1200 p.s.i.g., and more desirably in the neighborhood of 1500–2000 p.s.i.g., or higher. The investment cost for a partial oxidation hydrogen plant is substantially greater than for a natural gas-steam reforming hydrogen plant, in large part because there must be provided an air separation unit to supply pure oxygen, and a much larger amount of CO_2 is produced which must be removed from the H_2. The removal of this CO_2 is a costly operation by the usual techniques involving aqueous amine absorbents employed in low pressure, below 600 p.s.i.g., hydrogen plants. At the higher pressures, preferably employed in present invention, however, more economical CO_2 removal techniques can be used to greater advantage, involving the use of low temperatures below −10° F. A major part (60–90%) of the CO_2 can be condensed, with the liquid CO_2, when expanded at lower pressures, providing much of the refrigeration. Final cleanup with low viscosity, low freezing point, organic oxygen compounds such as acetone, methanol, and the like as absorbents is greatly facilitated, as the solubility of CO_2 in such solvents at high pressure and low temperature is greatly improved so less solvent must be heated, cooled, and circulated. Power can be generated from the expanding CO_2. The cost of gas compression is greatly reduced since only a relatively small volume of oxygen has to be compressed to provide a much larger volume of hydrogen already at the high pressure used. Thus a specific embodiment of the invention comprises the combination of high pressure partial oxidation of the residual portion of crude and low temperature removal of the CO_2 produced, using an organic oxygen compound liquid absorbent, preferably as a final cleanup after first condensing out part of the CO_2, with high pressure hydroconversion of the nonresidual portion of crude using the hydrogen so produced.

BRIEF DESCRIPTION OF THE DRAWING

Referring now to the attached drawing to further explain the invention, there is shown a simplified block flow diagram illustrating schematically the steps involved in the simplified refinery of the present invention.

DETAILED DESCRIPTION OF THE DRAWING

As shown in the drawing, a heavy sulfur-containing crude oil in line **11** is passed to crude distillation facilities in zone **12**, wherein straight run normally gaseous components of the crude are withdrawn as an overhead fraction in line **13**. A distillate fraction comprising essentially all of the normally liquid distillate portion of the crude, and having an end boiling point of at least 1000° F., is withdrawn in line **14**, leaving a vacuum residuum which is withdrawn through line **15**. The vacuum residuum passes to visbreaker **16** wherein it is mildly thermally cracked in a known manner producing gaseous by-products and additional distillates with minimal coke formation. The effluent of the visbreaking zone passes via line **17** to pitch stripper **18** wherein the gaseous and distillate portions are stripped out and returned via line **19** to the crude distillation facilities. The remaining visbroken pitch stripper tar in line **20** is withdrawn as feed to a partial oxidation process for hydrogen manufacture in hydrogen manufacturing zone **21**.

In hydrogen manufacturing zone **21** the stripped tar bottoms is reacted with molecular oxygen, nitrogen-free, supplied from an air fractionation unit through line **22**. The reaction is carried out in a noncatalytic combustion zone at temperatures of 2000–3000° F. using a stoichiometric deficiency of oxygen such that the combusted gas mixture comprises predominantly carbon monoxide and hydrogen, containing a small amount of elemental carbon, some carbon dioxide, hydrogen sulfide, and only a small portion of unreacted hydrocarbon. The combusted gas mixture is then worked up to provide high purity hydrogen in a known manner, involving removal of the car-

bon particles, shift conversion of the carbon monoxide by reaction with water to form carbon dioxide and hydrogen, and removal of the carbon dioxide and, usually, any remaining carbon monoxide. Sulfur compounds in the stripped tar bottoms appear as hydrogen sulfide, which is removed separately or with the carbon dioxide. These by-products may be withdrawn as a mixture, but preferably at least a major portion of the carbon dioxide is withdrawn as by line **23** as a high purity CO_2 stream which can be vented to the atmosphere, and there is also obtained a mixed gas stream of CO_2 and H_2S in line **24** having a sufficiently high H_2S concentration to serve as the feed gas to a sulfur recovery plant. This H_2S and CO_2 removal and separation can be accomplished by known processes, using for example a methanol absorbent.

The high purity hydrogen recovered in line **25** is divided into essentially two positions, a portion in line **26** being reacted with the distillate fraction of the crude petroleum in hydroconversion zone **28**, and the remaining portion of high purity hydrogen in line **27** being reacted with a portion of hydrofined distillate in hydrocracking reaction zone **29**.

In hydroconversion zone **28** the distillate fraction and the portion of high purity hydrogen, generally together with hydrogen-rich recycle gas, are passed into contact with a sulfactive hydrogenation catalyst at elevated temperatures in the range 650–850° F. and pressures in the range of 1500–4000 p.s.i.g., at throughput rates, based on the distillate fraction, of 0.2–10 volumes of oil per hour per volume of catalyst (LHSV) and, based on the total fresh and recycle hydrogen, of 2000–20,000 standard cubic feet of hydrogen-rich gas per barrel of oil. Net hydrogen consumption will be in the range 500–2000 s.c.f./bbl. The catalyst employed desirably comprises a Group VI metal or compound thereof, such as the sulfide, and a Group VIII metal or compound thereof, such as the sulfide, associated with a porous inorganic oxide carrier providing high surface area, such as alumina or combinations of alumina with silica, magnesia, zirconia, titania and the like. The catalysts are of the type which selectively promotes hydrodesulfurization and hydrodenitrogenation reactions, converting sulfur and nitrogen compounds in the oil to H_2S and NH_3, to form hydrofined distillate which is sufficiently sulfur- and nitrogen-free for recovery as distillate products, or at least sufficiently purified for the hereinafter-described subsequent hydrocracking. Typical suitable catalysts comprise nickel or cobalt together with molybdenum or tungsten dispersed in or on alumina, alumina with up to 50% silica, silica-magnesia, alumina-silica-zirconia-titania, etc. The catalysts can be prepared by known impregnation and coprecipitation methods.

The hydrofined distillate produced is passed via line **30** to distillation and recovery facilities in zone **31** wherein gaseous by-products are separated and removed through line **32**, and the distillate can, if desired, be separated into a gasoline boiling range fraction in line **33**, a kerosene or jet fuel boiling range fraction in line **34**, a middle distillate gas-oil fraction in line **35**, and a higher boiling gas-oil fraction in line **36**. Alternately, all or a portion of the hydrofined distillate may be passed via line **37** to zone **29**, but it is usually desirable to first remove part of the gaseous by-producsts.

At least a portion of the hydrofined distillate, desirably including the highest boiling portion, is passed as by line **36** and/or line **37** to hydrocracking reaction zone **29**, wherein the hydrofined distillate and the remaining portion of high purity hydrogen in line **29**, together with hydrogen-rich recycle gas, are passed into contact with an active hydrocracking catalyst at tempjeratures in the range 400-800° F., pressures in the range 1000–4000 p.s.i.g., at flow rates of oil relative to catalyst, flow rates of hydrogen relative to oil, and hydrogen consumption in the same ranges as described for hydroconversion zone **28**. The catalyst employed in hydrocracking zone **29** desirably is a catalyst of the type exhibiting substantially greater and more acidic hydrocrackling activity than the type used in zone **28**. Generally, the catalyst will comprise a Group VIII metal or compound thereof, such as the sulfide, e.g., cobalt, nickel, platinum, or palladium, associated with a porous inorganic oxide carrier having the properties of an active cracking catalyst, such as silica-alumina comprising 75–90% silica. The carrier may be, or may contain, aluminosilicate "molecular sieves" such as have been incorporated in cracking catalysts. Methods of preparing the catalysts are well known. The reactions promoted by this type of catalyst are of the type invloving a carbonium ion mechanism, wherein a characteristic is the production of a butane-rich fraction having a higher than equilbrium ratio of isobutane to normal butane accompanying the hydrocracking of the hydrofined fraction to hydrocracked lower boiling distillate of improved properties. To take maximum advantage in zone **29** of the activity of the hydrocracking catalysts, the hydroconversion in zone **28** is carried to the point of eliminating nitrogen compounds in the hydrofined distillate to below about 10 p.p.m. In many cases, however, it is advantageous to permit up to about 200 p.p.m. organic nitrogen to remain in the oil, and removal of the NH_3 formed is then not essential.

The hydrocracked distillate effluent of zone **29** is returned via line **38** to the distillation and recovery zone **31** for removal of gaseous by-products in line **32**. The sulfur-free distillate products recovered in lines **33**, **34**, and **35** thus comprise the hydrocracked distillate and any hydrofined distillate from zone **28** which was not hydrocracked in zone **29**.

The gaseous by-products in line **32** generally contain hydrogen sulfide produced in the hydrofining reactions occurring in zone **28**, and the gaseous fraction of line **13** from crude distillation zone **12** will also contain hydrogen sulfide liberated in the visbreaking and pitch stripping operations. These gaesous streams are passed to purification zone **39** wherein the hydrogen sulfide is removed and withdrawn through line **40**, providing a sulfur-free light gas stream in line **41**. The light gases can be utilized as sulfur-free fuel gas, including, desirably, the recovery of a portion thereof as liquefied petroleum gas. Ammonia and H_2S formed in zones **28** and **29** may be removed by water scrubbing, and may be recovered separately from the water in a manner now known.

The above-described simplified refinery scheme wherein the upgrading of the distillate portion of crude is carried out substantially entirely by hydrogen-consuming conversion reactions, with the hydrogen being provided by a partial oxidation which eliminates the residual portion of the crude, can be made self-balancing with respect to hydrogen production and consumption. Thus, in the case of a light, high gravity, crude oil feed, the fraction of crude separable as distillate in line **14** is greater relative to the amount of residue in line **20** as compared to the situation where the crude oil feed is a low gravity heavy crude. With the higher gravity crudes there is accordingly less residue available for use in manufacturing hydrogen. The distillates from high gravity crudes, however, usually require less hydrogen for upgrading as they tend inherently to require less severe hydrofining and hydrocracking. Conversely, in the case of low gravity crudes there is a larger amount of crude residue remaining for conversion to hydrogen, and more hydrogen is needed to upgrade the heavy, and usually highly contaminated, distillate fraction. Further, it will be recognized that the visbreaking and pitch stripping operations provide additional flexibility for providing more or less distillate via line **19** and more or less residue via line **20**.

The extent of upgrading by hydrofining and hydrocracking reactions in a conventional refinery scheme, wherein these processes were heretofore applied primarily as means of upgrading catalytic, coker, or thermal cycle oils, is either limited by the availability of hydrogen pro-

duced by catalytic reforming, or limited by the availability and cost of natural gas where the hydrogen is produced by steam-methane reforming. Accordingly, carrying the hydroconversion reactions to the optimum conversion for maximum upgrading was rarely practiced. In the present invention, however, the partial oxidation hydrogen manufacturing zone serves also as a means of disposing of the highest boiling residue of the crude by burning, wherein the H_2S produced is recovered, thus further justifying the use of partial oxidation in preference to other hydrogen manufacturing processes. In such a case, the availability of hydrogen becomes large enough such that the use of hydrofining and hydrocracking reactions as the sole means of upgrading the distillate portion of crude requiring desulfurization becomes practical and desirable. Furthermore, the hydroconversion reactions can be carried out at maximum hydrogen consumption for providing optimum upgrading to form truly sulfur-free distillate products.

The following example specifically illustrates one method of practicing the invention, and further describes details of various features in the steps involved. In the example, a crude oil is converted at 96% yield to sulfur-free C_5+ liquid products boiling below 650° F., with zero production of heavy fuel oil.

EXAMPLE

A heavy crude oil, 14° API, containing 1.1 weight percent sulfur and 0.77 weight percent nitrogen, is desalted, preheated, and fed to a vacuum distillation column operated at 2 p.s.i.a. An overhead fraction is withdrawn through the jet ejectors, cooled, and separated in a seal drum at about 2 p.s.i.g. and 90–100° F. into a normally gaseous fraction and condensed oil fraction having an end point of about 550° F. From the vacuum crude column there is withdrawn a top side cut boiling from about 550 to 650° F., a portion of which is cooled and returned as top reflux, and another minor portion of which is withdrawn as a straight-run diesel fuel. A lower side cut boiling from about 650 to 1050° F. is withdrawn from the vacuum crude column, and another heavier side cut boiling from about 850 to 1050° F. is withdrawn from lower in the column. The side cuts are cooled by heat exchange to the crude oil feed, thereby providing part of the feed preheat, and the 550–650° F. and 650–1050° F. side cuts are then combined with the fraction condensed from the overhead to form a single distillate fraction. The vacuum column bottoms amounts to about 30 volume percent of the crude oil feed, and a small portion of the bottoms is combined with a portion of the 850–1050° F. distillate cut for asphalt blending, the remainder of this distillate returning to the vacuum column for internal reflux. The remainder of the vacuum column bottoms, boiling substantially entirely above 1050° F., is fed to a visbreaker.

The vacuum column bottoms is heated in the visbreaker furnaces to about 900° F. at 200–250 p.s.i.g., which results in cracking to gas-oil distillate and lighter products in a yield of about 53 volume percent. The furnace effluent is quenched to about 750° F. to stop the reaction and then flashed sequentially in a high pressure flash drum and in a low pressure flash drum. Bottoms from the low pressure flash are heated to about 780° F. and passed to a tar stripper, or pitch stripper, wherein distillates are stripped out with superheated steam at about 3 p.s.i.a. The gases and vaporized distillates from the flash drums and tar stripper are returned to the vacuum column, whereby the normally gaseous by-products appear in the vacuum column overhead, and the normally liquid distillates appear ultimately in the single distillate fraction formed from the vacuum side cuts. The tar bottoms from the pitch stripper amounts to about 15 percent of the original crude oil, and this tar is fed to the hydrogen manufacturing unit.

In the hydrogen manufacturing unit the tar bottoms are dispersed in steam, preheated, and reacted with pure oxygen, supplied from an air fractionation plant, in a ceramic-lined reaction zone at a pressure of 1700 p.s.i.g. and a temperature of about 2600° F., the proportions of oxygen, steam, and tar bottoms being regulated such that this temperature is autogenously maintained. The resulting combusted gas mixture contains about 40–50% hydrogen, about 40–50% carbon monoxide, about 1 to 4% elemental carbon, about 3–10% carbon dioxide, less than about 1% methane, H_2S, and N_2. The hot gases leaving the partial oxidation reaction zone are immediately quenched with liquid water, which scrubs out the entrained carbon particles. Additional steam is added to the scrubbed gas mixture of carbon monoxide, hydrogen, hydrogen sulfide and carbon dioxide, and the mixture is passed into contact with a sulfur-tolerant shift conversion catalyst at a temperature of about 700–900° F. to convert the carbon monoxide to carbon dioxide with the simultaneous production of hydrogen. Carbon dioxide, unreacted steam, carbon monoxide and other impurities, including hydrogen sulfide formed from the sulfur compounds in the stripped tar bottoms, are removed from the shifted gas to produce high purity, 95–99%, hydrogen. (The nitrogen compounds in the tar appear as an N_2 diluent in the H_2.) The water is removed by condensation. The carbon dioxide and hydrogen sulfide are advantageously removed by partial condensation and by contacting at a low temperature, about −80° F., with liquid methanol. The methanol absorbent is regenerated in stages to release a pure carbon dioxide stream and a carbon dioxide-hydrogen sulfide mixture having a high enough H_2S concentration (about 12% H_2S—88% CO_2) to permit its use as feed to a conventional sulfur plant. Unconverted carbon monoxide is removed by catalytic conversion to methane. In the hydrogen manufacturing zone there is thus produced about 15,000 standard cubic feet of hydrogen per barrel of stripped tar bottoms fed to the partial oxidation. The hydrogen is compressed from about 1500 p.s.i.g. to about 3000 p.s.i.g. for use in the hydrofining and hydrocracking reactors.

The distillate fraction comprising the straight-run and visbreaker distillates is passed to a catalytic hydroconversion zone for hydrodesulfurization and hydrodenitrogenation, which is accompanied by some hydrocracking. The blended distillate feed has a gravity of about 18.5° API, boils from 150° to 1100° F., and contains one weight percent sulfur and nearly 5000 p.p.m. nitrogen. The distillate fraction and about 10,000 s.c.f. of hydrogen-rich gas per barrel, including makeup hydrogen from the hydrogen manufacturing zone, are passed at about 750° F. and 3000 p.s.i. downflow through a reactor containing fixed beds of nickel sulfide-tungsten sulfide-alumina-silica catalyst particles at 0.85 LHSV. About 1500 standard cubic feet of hydrogen per barrel of feed is consumed in the hydroconversion reactions resulting. The effluent of the reactor is cooled and water washed at the high pressure to remove the ammonia and a portion of the hydrogen sulfide formed. The hydrogen-rich gas is recycled, and the liquid oil is then flashed at a lower pressure to remove dissolved normally gaseous by-products. The oil is then passed to distillation facilities wherein an overhead cut boiling below 200° F. is separated and liquid distillate cuts are formed, comprising 200–300° F. gasoline, 320–400° F. jet fuel, 400–500° F. kerosene, 500–650° F. diesel fuel, and a 650° F.+bottoms fraction. The gasoline cut contains only one p.p.m. sulfur and 0.5 p.p.m. nitrogen. All of the side cuts are essentially sulfur-free, containing less than 100 p.p.m. sulfur, and the 650° F.+bottoms cut contains only 3 p.p.m. nitrogen.

The 650° F.+bottoms and a portion of the 500–650° F. diesel fuel cut are combined and passed to a catalytic hydrocracking zone with about 6000 standard cubic feet of hydrogen-rich gas per barrel, including makeup hydrogen from the hydrogen manufacturing zone, at about 675° F. and 3000 p.s.i.g. to contact in a reactor a nickel sulfide-silica-alumina catalyst at 0.5 LHSV. About 60 volume per-

cent of the gross feed is converted to distillates boiling below 500° F. Hydrogen consumption is about 1500 s.c.f. per barrel of feed converted. The reactor effluent is cooled at the high pressure to separate hydrogen-rich recycle gas, and the oil is then flashed at a lower pressure to separate dissolved normally gaseous hydrocarbons. The hydrocracked oil is then returned to the distillation facilities together with the effluent of the hydroconversion reactor for recovery of the described products.

The normally gaseous fraction from the vacuum crude column and the gaseous fraction from the distillation of the hydroconversion zone and hydrocracking zone effluents are combined and passed to a gas recovery zone to separate an H_2S-containing light gas stream from propane, butanes, isopentane, and a C_5–200° F. cut for gasoline blending. The H_2S in the liquid propane and in the light gas stream is absorbed in an aqueous monoethanolamine solution. The recovered H_2S is stripped from the MEA in a reboiled regenerator and is sent to a sulfur plant for conversion to elemental sulfur. Residual H_2S is removed from the propane product to meet LPG specifications by adsorption in a molecular sieve adsorption unit.

From 1000 barrels of heavy crude oil feed there are recovered as products about 2 tons of sulfur, 1600 pounds of NH_3, 120 barrels of propane and butanes, 460 barrels of motor gasoline, about 380 barrels of jet fuel, and about 120 barrels of stove oil and diesel gas oil. The 200–320° F. gasoline cut is passed to a catalytic reformer, and the hydrogen produced therein is combined with the hydrogen produced in the partial oxidation hydrogen manufacturing unit, reformer hydrogen amounting to about 10% of the total. Heat liberated in the hydroconversion and hydrocracking zones is used to generate steam, and extensive use is made of power recoverey turbines on high pressure streams, to supply nearly 70% of the power requirements of the partial oxidation hydrogen plant. The remainder of the total power requirements of the process is provided by a gas turbine generator, the hot combustion gases from which are exhausted into a high pressure boiler supplying 1700 p.s.i. steam to the partial oxidation unit. Overall steam production and consumption are entirely in balance.

For comparison with the foregoing example wherein there is zero heavy fuel oil production and 96% yield of sulfur-free light distillates besides propane and butanes, in a prior art refinery scheme applied to the same crude oil using vacuum crude distillation in combination with catalytic cracking of gas oils and thermal cracking of residua, the yield of light distillate is only 48% and of heavy fuel oil is 47%. By adding units for hydrofining and hydrocracking of the cracked cycle gas oils, the light distillate yield is raised to 59% and the fuel oil yield is lowered to 40%. In a combination of vacuum crude distillation, visbreaking, and pitch stripping with hydrofining and hydrocracking of the distillates, wherein the hydrogen is supplied by steam-natural gas reforming, the light distillate yield is 78% and fuel oil 30% (tar bottoms plus gas oil cutter).

It is within the contemplation of the present invention that minor portions of the original crude oil feed or of the gaseous, distillate, or residual fractions may be withdrawn from the process if suitable for use in products which are not required to have a low sulfur content. For example as described in the example, part of the vacuum residuum, or the pitch stripper bottoms, may be used in asphalt manufacture, and part of a heavy distillate fraction may be used as a blending or cutter stock. Also, a portion of sulfur-containing straight-run distillate fraction may bypass the hydrofining and hydrocracking zones for blending with a sulfur-free distillate product of the process, to provide a fuel oil having a satisfactorily low sulfur content. Thus when it is stated that the crude oil is converted "substantially entirely" to sulfur-free distillate products and gaseous by-products in the process of the invention, the intended meaning is that no more than about 10% of the crude or fractions thereof will be otherwise processed. In the foregoing example, for instance, the total of streams so withdrawn for asphalt, cutter, and diesel fuel amounts to less than 4% of the crude.

Persons skilled in the art will recognize that it is within the intended scope of the invention to carry out the crude separation into the distillate and residual fractions by other means equivalent to the methods specifically described herein. Thus, the crude may be distilled in several steps and multiple columns, including atmospheric and vacuum distillation columns. Th amount of the residuum fraction may be reduced by other means equivalent to visbreaking and tar or pitch stripping for providing additional distillate fraction. The hydrofining and hydrocracking may be carried out in a variety of ways besides downflow of hydrogen and oil through fixed beds of catalyst in reactors. For example, there may be used concurrent upflow of gas and oil or countercurrent flow, and the catalyst may gravitate or be fluidized or maintained in a liquid slurry. Multiple reactors in series or parallel can be used, portions of the crude distillate can be separately treated, and separate distillation facilities may be used for the recovery of light distillates from the hydrofined oil and the hydrocracked oil. The hydrofined oil may pass directly to the hydrocracking zone. Various arrangements of multiple columns can be used in working up the products. In the train of steps in the hydrogen manufacturing plant using partial oxidation, any of a variety of known means for removing, recovering, and recycling the carbon formed can be incorporated. High pressure steam can be generated, and more than one stage of shift conversion and/or CO_2 removal can be provided. Improved shift conversion catalysts are commercially available such that a later stage of shift conversion can be carried out at a lower temperature of 400–700° F. after an earlier higher temperature stage, and the CO_2 and H_2S can be removed in stages using different kown absorbents. Residual CO can be left in the H_2 in some cases, or it can be removed by absorption in cuprous solutions such as copper ammonium acetate. The specific mode of operating the overall process described in detail herein, however, has distinct advantages of simplicity, low operating cost, and optimum energy integration uniquely fulfilling that object of the invention, to provide a simplified refinery.

I claim:

1. A process for converting sulfur-containing crude oil substantially entirely to sulfur-free distillate products and gaseous by-products, comprising:

(1) separating the crude oil into essentially three fractions, (a) a normally gaseous fraction, (b) a sulfur-containing distillate fraction, and (c) a sulfur-containing residual fraction;

(2) reacting the sulfur-containing residual fraction with molecular oxygen at partial oxidation conditions for synthesis gas generation in a hydrogen manufacturing zone to obtain raw hydrogen-rich gas, shift converting CO contained in the raw hydrogen-rich gas to CO_2, and then removing H_2S and CO_2 from the raw hydrogen-rich gas to provide high purity hydrogen;

(3) reacting the sulfur-containing distillate fraction with a portion of said high purity hydrogen in contact with a sulfactive hydrogenation catalyst at elevated temperature and pressure in a hydroconversion zone, converting sulfur in said distillate to H_2S and forming hydrofined distillate and gaseous by-products;

(4) reacting at least a portion of said hydrofined distillate with the remaining portion of said high purity hydrogen in contact with an active hydrocracking catalyst at elevated temperature and pressure in a hydroconversion zone, converting hydrofined distillate to hydrocracked lower boiling distillate and forming gaseous by-products;

(5) removing H_2S from the distillates and the gaseous by-products obtained from each of the hydroconversion zones, recovering gaseous by-products, and recovering substantially sulfur-free distillate products comprising hydrocracked distillate and any hydrofined distillate not hydrocracked.

2. A process in accordance with claim 1 wherein the crude oil is separated into the three fractions by a combination of distilling the crude under vacuum, visbreaking vacuum distillation bottoms, and stripping gaseous by-products and additional sulfur-containing distillate from the visbreaker effluent in a pitch stripper, forming the sulfur-containing residual fraction comprising pitch stripper bottoms.

3. A process in accordance with claim 1 in combination with catalytically reforming a portion of sulfur-free distillate produced, and augmenting said high purity hydrogen with hydrogen produced in the catalytic reforming.

4. A process which comprises (a) separating a sulfur-containing crude oil into a distillate fraction and a residual fraction; (b) partially oxidizing the entire residual fraction with molecular oxygen at an elevated pressure of at least 1500 p.s.i.g. and temperature conditions for synthesis gas generation in a hydrogen manufacturing zone, shift converting the CO in the gas produced to CO_2, and removing H_2S and CO_2 to provide high purity hydrogen by contacting the shifted gas at the elevated pressure with an organic oxygen compound liquid absorbent at a temperature below —10° F.; and (c) reacting the sulfur-containing distillate fraction with a portion of said high purity hydrogen in contact with a sulfactive hydrogenation catalyst at elevated temperature and pressure in a hydroconversion zone, converting sulfur in said distillate to H_2S and forming hydrofined distillate and gaseous by-products; and reacting at least a portion of said hydrofined distillate with the remaining portion of said high purity hydrogen in contact with an active hydrocracking catalyst at elevated temperature and pressure in a hydroconversion zone, converting hydrofined distillate to hydrocracked lower boiling distillate and forming gaseous by-products.

5. A process in accordance with claim 4 wherein in the hydrogen manufacturing zone a portion of the CO_2 produced is removed by condensation from the shifted gas, and the remaining portion is removed by contacting with the organic oxygen compound.

References Cited

UNITED STATES PATENTS

3,008,895	11/1961	Hansford et al.	208—68
3,012,962	12/1961	Dygert	208—154
3,120,993	2/1964	Thormann et al.	23—2
3,380,910	4/1968	Griffiths	208—58
2,911,352	11/1959	Goretta et al.	208—68
3,240,694	11/1963	Mason et al.	208—59
3,254,020	5/1966	Frayer et al.	208—89

DELBERT E. GANTZ, Primary Examiner

T. H. YOUNG, Assistant Examiner

U.S. Cl. X.R.

208—58, 92

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,537,977 Dated November 3, 1970

Inventor(s) CALVIN S. SMITH, JR.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 68, "Table II" should read --Table III--.

SIGNED AND
SEALED
MAR 9 1971

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents