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## HYDROCARBON CONVERSION PROCESS

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This invention relates generally to the refining of crude petroleum and residua and more particularly relates to a new and improved process for refining crude petroleum wherein an external source of hydrogen has been eliminated.

The upgrading of petroleum stocks by catalytic processing in the presence of hydrogen has been known for many years but its effectiveness has been somewhat limited by the relatively high cost of hydrogen production. While new methods for producing hydrogen have greatly decreased the cost in recent years, this problem is nonetheless still present.

The process of this invention makes use of two important principles in order to eliminate the use of externally supplied hydrogen. In the first instance crude petroleum normally having a high carbon-hydrogen ratio is first subjected to high temperature coking in order to produce a cracked distillate having a lower carbon-hydrogen ratio and which is at the same time more amenable to upgrading by hydrogenation. In the second instance the process employs straight run distillates of the gasoline boiling range, such as are normally available in fair quantity in a modern refinery, in order to adjust the hydrogen requirements. This is accomplished in a reforming step wherein the coker distillate, following a desulfurization step, is reformed simultaneously with the straight run fraction. The flow of straight run to the reforming step is regulated and controlled by the hydrogen requirements of the preceding desulfurization stage.

It is an object of this invention to refine crude petroleum and to obtain a maximum yield of low boiling petroleum fractions and with a minimum yield of less desirable products.

It is another object of this invention to refine crude petroleum by means of catalytic desulfurization and hydrogenation wherein no external source of hydrogen is required.

It is another object of this invention to simultaneously reform straight run and desulfurized coker distillate fractions whereby a hydrogen-rich stream is obtained which supplies the hydrogen requirements of the preceding desulfurization stage.

It is another object of this invention to simultaneously refine crude oil and upgrade straight run gasoline.

It is another object of this invention to dilute desulfurized coker distillate fractions with a straight run stock in order to dilute the nitrogen content of the desulfurized fraction and thereby minimize nitrogen poisoning during a subsequent reforming step.

Briefly, this invention relates to a three-step process in the refining of crude oil, namely the sequence of coking, desulfurization and reform-

ing. The coking step is any conventional process such as delayed coking for the conversion of the oil into gases, vapors boiling below a given end point, and solid coke. In an optional step of the process the coker distillate may be subjected to additional cracking such as in a thermal or catalytic cracker in order to reduce the boiling range of the stock. The preceding coking step serves primarily to reduce the carbon-hydrogen ratio of the fractions to be subjected to subsequent processing. The coker distillate, together with any cracked derivatives, is subjected to desulfurization step in the presence of a cobalt molybdate catalyst whereby hydrogenation of olefins, sulfur removal and nitrogen removal are simultaneously effected. In the preferred modification the desulfurization step is effected at such temperatures as to minimize the synthesis of aromatics, which synthesis is accompanied by increased carbon deposition. The desulfurized product is first mixed with a straight run gasoline fraction and is then subjected to reforming in the presence of a platinum-alumina catalyst. The reforming step is of such character that extensive dehydrogenation and aromatization of the charge stock occurs with consequent hydrogen production. The hydrogen produced in the reforming step is mixed with the unreacted hydrogen of the desulfurization step and is subjected to separation by hypersorption, for example, in order to produce a hydrogen-rich recycle stream which in part flows as recycle hydrogen to the reforming step, and which in part flows as recycle hydrogen to the desulfurization step. Such reforming in the presence of hydrogen is also referred to as "hydroforming," and such desulfurization in the presence of hydrogen is also referred to as "hydro-desulfurization."

The cobalt molybdate catalyst which has been found to be effective in the process of this invention comprises a mixture of cobalt and molybdenum oxides wherein the molecular ratio of CoO to MoO<sub>3</sub> is between about 0.4 and 5.0. This catalyst may be employed in unsupported form or, alternatively, it may be distended on a suitable carrier such as alumina, silica, zirconia, thoria, magnesia, magnesium hydroxide, titania or any combination thereof. Of the foregoing carriers it has been found that the preferred carrier material is alumina and especially alumina containing about 3-8% by weight of silica.

In the preparation of the unsupported cobalt molybdate catalyst the catalyst can be coprecipitated by mixing aqueous solutions of, for example, cobalt nitrate and ammonium molybdate, whereby a precipitate is formed. The precipitate is filtered, washed, dried and finally activated by heating to about 500° C. Alternatively, the cobalt molybdate may be supported on alumina by coprecipitating a mixture of cobalt, aluminum

and molybdenum oxides. A suitable hydrogel of the three components can be prepared by adding an ammoniacal ammonium molybdate solution to an aqueous solution of cobalt and aluminum nitrates. The precipitate which results is washed, dried and activated. In still another method a washed aluminum hydrogel is suspended in an aqueous solution of cobalt nitrate and an ammoniacal solution of ammonium molybdate is added thereto. By this means a cobalt molybdate gel is precipitated on the alumina gel carrier. Catalyst preparations similar in nature to these and which can also be employed in this invention have been described in U. S. Patents 2,369,432 and 2,325,033.

Still other methods of catalyst preparation may be employed such as by impregnating dried carrier material, e. g. an alumina-silica gel, with an ammoniacal solution of cobalt nitrate and ammonium molybdate. Preparations of this type of cobalt molybdate catalyst are described in U. S. Patent 2,486,361. In yet another method for preparing impregnated molybdate catalyst the carrier material may be first impregnated with an aqueous solution of cobalt nitrate and thereafter impregnated with an ammoniacal molybdate. Alternatively, the carrier may also be impregnated with both solutions in reverse order. Following the impregnation of the carrier by any of the foregoing methods the material is drained, dried and finally activated in substantially the same manner as is employed for the other catalysts. In the preparation of impregnated catalysts where separate solutions of cobalt and molybdenum are employed, it has been found that it is preferable to impregnate the carrier first with molybdenum, e. g., ammoniacal ammonium molybdate, and thereafter to impregnate with cobalt, e. g., aqueous cobalt nitrate, rather than in reverse order.

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

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

It is apparent from the foregoing description of the different types of cobalt molybdate catalyst which may be employed in this invention that we may employ either an unsupported catalyst, in which case the active agents approximate 100% of the composition or we may employ a supported catalyst wherein the active agents, cobalt and molybdenum oxides, will generally comprise from about 7 to 22% by weight of the catalyst composition. In all of the foregoing catalytic preparations it is desirable to maintain the molecular ratio of cobalt oxide as CoO to molybdc oxide as MoO<sub>3</sub> between about 0.4 and 5.0.

The desulfurization catalyst may be employed

at temperatures between about 700° and 1000° F. However, it is preferable that temperatures in the range of about 750° to 850° F. be employed since under these conditions there is a minimum build-up of carbon on the catalyst and such conditions therefore permit long on-stream operating periods before regeneration becomes necessary, such as up to 200 hours or more. Suitable pressures range from about 500 to 10,000 and preferably from about 1000 to 2000 pounds per square inch. Feed rates from about 0.1 to 10.0 and preferably between 0.4 and 2.0 volumes of liquid feed stock per volume of catalyst per hour are employed in the desulfurization stage. About 1000 to 10,000 cu. ft. of recycle or fresh hydrogen are employed per barrel of feed.

The process of the present invention may be effected in any suitable equipment, a particularly satisfactory system comprising a fixed bed process in which the catalyst is disposed in one or more reaction zones and the unsaturated fraction to be hydrogenated is passed therethrough either in upward or downward flow and either concurrently or countercurrently to a stream of hydrogen. Fluidized type process in which the catalyst is carried into the reaction zone by the unsaturated fraction and/or hydrogen and maintained in a state of turbulence in the reaction zone under hindered settling conditions, moving bed type process in which the reactants are passed concurrently or countercurrently to a moving bed of catalyst, or the suspensoid type operation in which the catalyst is carried as a slurry in the reactants, may also be employed. Conventional processes using guard reactors to remove impurities from the charging stock prior to the hydrogenation treatment may be employed if desired.

The reforming catalyst of the present invention is a platinum catalyst preferably supported on alumina and which contains between about 0.5 and 8% by weight of combined halogen. Preferably the catalyst should contain between about 0.01 and 1.0% by weight of platinum. While alumina is the preferred support, it may also be supported on the carriers described hereinbefore in connection with cobalt molybdate catalysts. In the preferred method for preparing the reforming catalyst the halogen, which is preferably fluorine or chlorine, is incorporated into the alumina prior to comingling or deposition of the platinum thereon. In the preferred modification a wet alumina gel is comingled with the requisite amount of hydrogen chloride and is thereafter comingled in the wet state with a solution of chloroplatinic acid which has been treated with hydrogen sulfide. The composite is filtered, dried and heated to a temperature between about 800° and 1200° F. and preferably in the presence of hydrogen.

The alumina gel of this invention employed for supporting the platinum may be prepared by any of the methods well known in the art, such as by treating any water-soluble alumina salts with either acids or bases in order to cause the precipitation of aluminum hydroxide. In the preferred modification halogen-containing aluminum salts such as either aluminum chloride or aluminum fluoride are treated with ammonia or other alkaline reagent to cause precipitation of the gel, which normally contains appreciable amounts of halogens which are sufficiently combined that they are removable only upon extended washing with fresh water. Gels of this type may be mixed with hydrogen sulfided chloroplatinic acid mixture or, alternatively, such gels may be

treated at temperatures up to 1300° F. and thereafter impregnated with aqueous solutions of platinum-containing materials such as chloroplatinic acid.

Where the alumina gel is comingled with the platinum-containing compound it is filtered to a dry cake and dried at low temperatures such as in the range of 200° to 400° F. Following the initial drying the catalyst can be formed into pills, etc. in much the same manner as has been described hereinbefore in connection with the desulfurization catalyst.

The reforming step is carried out at temperatures between about 850° and 1050° F. and preferably in the range of 900° to 1000° F. A pressure in the range of about 50 to 1000 pounds per square inch is employed in conjunction with a liquid hourly space velocity between about 0.1 and 10 and preferably between about 0.4 and 2.0. Recycle hydrogen amounting to between 1000 and 10,000 cu. ft. per barrel of charge stock is introduced with the charge stock to minimize carbon deposition. Operating cycles of up to several months may be employed between regenerations.

Perhaps the process of this invention can best be understood by reference to the attached figure.

The feed stock to the process may be any full range crude oil, reduced residuum, shale oil or the like. Such feed stock flows through line 11 to pump 12 thence through line 13, interchanger 14 and line 15 to preliminary fractionating tower 16. Fractionating tower 16 produces an overhead fractionated product to line 17 which is passed through lines 121 or 122 as will be described hereinafter. Topped feed stock flows from the bottom of fractionating tower 16 through line 18 to heater 19 wherein it is heated to a suitable coking temperature such as in the range of 800° to 1000° F. Heated oil from heater 19 flows through line 20 to coking unit 21.

Coking unit 21 is of any suitable conventional design for converting petroleum oils into gases and vapors boiling below a particular end point and producing a solid residue of coke. Such coking unit may be of the delayed coking type wherein coke is accumulated during a coking period of 15 minutes to 2 hours, for example, and is then removed by suitable means such as with a stream of high velocity water in the well known hydraulic decoking method. In such cases coker 21 represents one of several coking vessels which are employed in sequence for coking and decoking whereby a continuous flow of feed and products may be maintained. In another modification coker 21 may be of the continuous type wherein the oil is continuously passed through a bed of heated pellets of coke or other solid heat transfer material thereby depositing a layer of coke upon such pellets. The pellets containing added coke are removed and may be burned in order to recover the heat value of the coke and form additional hot pellets for further coking, or such pellets may be screened to recover the smaller pellets which are reheated and returned to the coking zone. In general such coking operations are effected at relatively low pressures such as in the range of atmospheric to 100 pounds per square inch.

Coke is shown in the attached figure as being discharged from vessel 21 through line 22 by any of the foregoing methods. Coker distillate is removed from vessel 21 through line 23 whence it passes through condenser 24 into line 25 and

thence to fractionating tower 26. The overhead from fractionating tower 26 passes through lines 27 and 28 into the fuel gas recovery system. Fractionating tower 26 discharges gasoline boiling range stock through line 29, light gas oil through line 30 and heavy gas oil through line 31. Light gas oil in line 30 may be joined with the gasoline in line 29 by opening valve 32. Light gas oil in line 30 may be joined with heavy gas oil in line 31 by opening valve 33.

In the preferred method of operation heavy gas oil from fractionator 26 passes through line 31 to heater 34 which is operated under sufficient temperature and pressure to effect at least a partial cracking of the heavy gas oil flowing therethrough. Cracked products from heater 34 flows through line 35 and are cooled in condenser 36 whence they flow through line 37 to fractionating tower 38. Gaseous products of the cracking operation pass overhead from fractionating tower 38 through line 39 whence they join light gaseous cracked products from the coking step and flow through line 28 to the fuel gas recovery system. The heavy bottoms from fractionating tower 38 discharged through line 40, valve 41 and line 42 to fuel oil storage not shown. In one modification of the invention the uncracked bottoms from fractionating tower 38 flow, upon the closing of valve 41, through line 43, valve 44 and line 45 to pump 46 whence they are forced into line 47 and join in line 18 the topped feed stock flowing to heater 19 as charge stock to coker 21.

While a thermal cracker 34 is shown, such may be replaced with a catalytic cracker if such is desired. Catalytically cracked vapors are then supplied to condenser 36 and fractionating tower 36 as shown.

The gasoline boiling range stock from the cracking operation is withdrawn from fractionating tower 38 through line 48 and joins with the coker gasoline flowing in line 29 whence the products flow through line 49 to heater 50. In the preferred modification, light gas oil from fractionating tower 26 is caused to flow from line 30, by the closing of valve 33 and the opening of valve 32, into line 29 whence it flows through line 49 into heater 50. Recycle hydrogen is supplied with the charge to heater 50 through line 51 as described hereinafter. Effluent from heater 50 discharges through line 52 into desulfurization reactor 53 wherein it is contacted with a cobalt molybdate desulfurization catalyst of the type described hereinbefore. Desulfurization reactor effluent flows through line 54, condenser 55 and line 56 into fractionating tower 57.

The bottoms of fractionating tower 57 comprises desulfurized and hydrogenated light gas oil, the latter being suitable for diesel engine fuel without further refining. Fractionating tower 57 is suitably controlled so that the initial boiling point of the bottoms product is in the range of 400° to 500° F., preferably. Bottoms product from fractionating tower 57 flows through line 58, valve 59 and line 60 to diesel fuel storage not shown.

Alternatively, the bottoms product from fractionating tower 58 may be recycled, if desired, to the cracking step. This is accomplished by closing valve 59 whence the product flows from line 58 through line 61, valve 62 and line 63 into pump 64 whence it flows through line 65 and joins the charge stock to thermal cracking heater 34.

The overhead from fractionating tower 57 is

preferably controlled to include propane, propene and lighter and is removed through line 66 and valve 67 and line 68 whence it flows to the hydrogen recovery system described hereinafter. The partial closing of valve 67 diverts a part of the gaseous stream from line 66 through hydrogen analyzer controller recorder 69 which is in turn employed to actuate motor valve 70 as described hereinafter.

The C<sub>4</sub> to 400-500° F. fraction from fractionating tower 57 flows through line 71 to heater 72. Recycle hydrogen from line 73 joins the gasoline range stock flowing to heater 72. Effluent of heater 72 flows through line 74 into catalytic reformer 75.

Catalytic reformer 75 employs a platinum-alumina reforming catalyst of the type and under the conditions described hereinbefore. Reformer effluent flows through line 76, through heat exchanger 77 and line 78 into gas-liquid separator 79. Hydrogen-rich gas from gas-liquid separator 79 flows through line 84 to the hydrogen recovery system described hereinafter. Liquid from gas-liquid separator 79 is removed under control of a liquid level control not shown through line 80, heat exchanger 81 and line 82 whence it passes into fractionating tower 83.

Fractionating tower 83 is a rerun tower for the reformed gasoline boiling range product. Finished gasoline flows from fractionating tower 83 as the overhead through line 85 to product storage not shown. Bottoms product from fractionating tower 83 comprises small amounts of polymer and other miscellaneous products. Polymer is removed from rerun tower 83 through line 86, valve 87 and line 88 to polymer storage. If desired, such polymer may be recycled to the cracking step by closing valve 87 whereupon the product flows through line 89, open valve 90, line 91 when it enters pump 92 and is forced into line 93 whence it flows through line 65 to heater charge flowing to heater 34.

Referring now more particularly to the hydrogen recovery system, hydrogen-rich gas from the desulfurization step in line 68 and hydrogen-rich gas from the reforming step in line 84 are joined in line 94 whence they flow through valve 95 and line 96 as charge stock to hypersorption unit 98. The pinching of valve 95 causes a part of hydrogen-rich gas in line 94 to be diverted through hydrogen analyzer controller recorder 98 which may be employed to actuate motor valve 70 as described hereinafter.

Hypersorption unit 98 is of the type such as is shown in U. S. Patent 2,519,873 and consists of an adsorption zone, a rectification zone, a stripper, charcoal rate controller and a lift line 99. Hydrogen-rich gas entering through line 97 passes upwardly through cold charcoal which absorbs C<sub>1</sub> and heavier fractions, permitting the hydrogen to remain substantially unadsorbed. The hydrogen passes upwardly through the bed and is removed through line 100. The charcoal containing adsorbed methane and heavier constituents flows downwardly from the adsorption zone and enters the rectification zone, the lower portion of which comprises a stripping zone. The application of heat to the charcoal in the stripping zone causes the gases to be partially desorbed from the adsorbent and to pass upwardly through the descending charcoal whence it contacts cooler charcoal and causes an exchange of heavier for lighter constituents in the manner of rectification. Following rectification the charcoal containing methane and heavier con-

stituents is thereafter heated to a temperature sufficient to cause the remaining gases to be desorbed whereupon they are removed through line 101 and pass to fuel gas storage not shown. Heated charcoal from the stripper flows through a charcoal regulator which controls the volume of charcoal dropping therethrough per unit time to some desired rate. Charcoal from the charcoal regulator passes downwardly through line 102 whence it is lifted through lift line 99 and is returned to the top of the hypersorber. Such lifting may be effected in any suitable manner such as by gas lifting or mechanical elevators. At the top of the hypersorber the heated charcoal is cooled to condition it for absorption of additional gas.

In another modification of the invention the hypersorber may be employed in a side cutting operation so as to produce a C<sub>1</sub>-C<sub>2</sub>-rich stream through line 103 by opening valve 104 whence it flows into line 105 to storage. By employing this method a C<sub>3</sub>-H<sub>2</sub>S-rich stream may be produced through line 101. This method is optional, however.

The gas flowing in line 84 from the reformer will generally contain 80-90 volume per cent of hydrogen and the gas flowing in line 68 from the desulfurizing unit will generally contain only 20-50 volume per cent of hydrogen. Such gases may therefore be introduced into the hypersorber at two separate feed engaging zones. Thus by closing valve 141 and opening valve 142 about 20-50 volume per cent hydrogen is introduced in lower feed line 97 while 80-90 volume per cent hydrogen flows through valve 142 and upper feed line 143 into an upper feed engaging zone. By this method lean hydrogen is introduced lower in the tower so as to contact a greater amount of charcoal and rich hydrogen is introduced higher up so as to contact less charcoal. A lower total flow of charcoal is needed to make a given separation thereby.

Hydrogen in line 100 flows through flow controller recorder 106 which may be employed to actuate motor valve 70. Hydrogen thereafter flows through line 140 and line 73 to provide a recycle for the catalytic reformer and through line 140 and line 51 to provide a recycle for the desulfurization reactor.

The hydrogen content of the make gas from reformer reactor 75 flowing in line 84 is usually 80 to 90 volume per cent and such gas may be employed as recycle gas to either the desulfurization reactor 53, or to reformer reactor 75 or to both. For this purpose valve 139 is opened and compressor 138 then takes suction on line 84 and forces make gas into line 140 whence it passes to the reformer heater 72 or through line 51 to the desulfurization reactor heater 50.

In another modification of the invention the make gas from the desulfurization reactor 53 and the reformer reactor 75 are recycled, the former being passed from line 94 through valve 141 and valve 139 to compressor 138 and the latter from line 84, valve 139 and compressor 138. For this purpose the net make gas is taken through valve 95 to the hypersorber and processed to recover the hydrogen content and the hydrogen is returned through line 100 and orifice plate 106 to line 140.

Referring now more particularly to fuel gas recovery system, cracked gases from the coker and thermal cracker flow through line 28 and line 107 to compressor 108. These cracked gases contain moderate amounts of hydrogen which

may be recovered if desired. Other waste refinery gases containing hydrogen, e. g., catalytic cracked off gases, may be passed through line 109a by opening valve 110a into line 111 which joins line 107 passing to compressor 108. Effluent gases from compressor 108 flow through line 109 to gas-liquid separator 110. Liquid from gas-liquid separator 110 is removed through line 112 whence it flows to line 49 to join the heater charge to heater 50. Alternatively, compressed liquids may be discharged through line 150 by opening valve 151. Gas from gas-liquid separator 110 passes overhead through line 113 and line 114 whence they are sent to fuel gas storage not shown. If it is desired to recover hydrogen from such gas, it is then passed from line 113 into line 115, opened valve 116 and line 117 into line 97 whence it joins the charge to hypersorber 98 and is handled as described herebefore.

Referring now more particularly to the addition of straight run to the charge stock flowing to the catalytic reformer 75, straight run gasoline boiling range stock is introduced through line 118 whence it flows through motor valve 70 and line 119 into line 71. Where it is desired to augment the straight run stock with the straight run from the crude oil feed valve 120 may be opened whereby line 118 is connected through line 121 with line 17 containing the topped straight run distillate of the crude.

The flow of straight run to the catalytic reformer through line 118 is controlled by motor valve 70. Motor valve 70 in turn may be controlled through any one of three controllers. Hydrogen analyzer recorder controller 69 determines the hydrogen content of the gaseous components from the desulfurization reactor 53. Such gases are generally in the range of 25 to 50% by volume of hydrogen. Thus by setting the hydrogen controller recorder 69 to control the hydrogen concentration of the gas in line 56 at some definite value, normally closed motor valve 70 will be opened to permit a greater flow of straight run to reformer 75 as the hydrogen concentration of the off-gas of desulfurizer 53 decreases, and vice versa. Alternatively, motor valve 70 may be controlled by hydrogen analyzer controller recorder 98 which determines the hydrogen concentration of the combined off-gas from the desulfurizer 53 and the reformer 75 which flows through line 94. As still another alternative, motor valve 70 may be controlled by flow recorder controller 106 which is actuated by the volume of hydrogen produced from hypersorber 98 through line 100. In all such cases or in other possible combinations the concentration of hydrogen or the volume of hydrogen or both in the entire system or parts thereof may be employed to control the amount of straight run supplied to the remainder to maintain the system in hydrogen balance. If, in the fractionation of crude oil in fractionator 16, the amount of straight-run which is taken overhead and passed to reformer 75 via lines 17 and 122, heater 50, desulfurizer 53, fractionator 57, line 71 and heater 72 is sufficient to maintain the system in hydrogen balance, the hydrogen controls just described will cause motor valve 70 to remain closed; otherwise valve 70 will be opened as described above to permit further addition of straight-run gasoline through line 118.

In an alternative operation where it is desired to feed straight run from the topped crude to the

desulfurization reactor, valve 120 may be closed so that such overhead distillate from fractionating tower 16 will then flow through line 122 and opened valve 123 whence it flows through line 124 to line 49 and joins the heater charge to heater 50. Under this type of operation fractionating tower 16 may be operated to produce straight run gas oils overhead whereby such straight run stocks by-pass coking and cracking operations.

In still another modification the entire coker distillate in line 23 may be withdrawn through line 125, opened valve 126 and line 127 whence it joins line 124 and flows as the charge stock in whole or in part to heater 50.

Perhaps the application of this invention can best be understood by reference to the following specific example.

#### Example

About 14,400 B./D. of a crude oil containing about 5.5% by weight of sulfur and 0.3% by weight of nitrogen are subjected to a delayed thermal coking process whereupon there is produced the following products (B./D. refers to barrels per day):

	B./D.
Pressure distillate and straight run, 400° F. end point	3090
Light gas oil, 400-700° F.	5300
Heavy gas oil	3368

The heavy gas oil from the foregoing operation is subjected to thermal cracking whereupon there is produced the following products:

	B./D.
Pressure distillate, 400° F. end point	896
Fuel oil	2180

The pressure distillate from the cracking is combined with the pressure distillate and straight run and light gas oil from the coking step, making a total volume rate of 9286 B./D. which was then subjected to desulfurization at about 800° F. and 1500 p. s. i. with the addition of 3000 cu. ft. per barrel of hydrogen recycle. About 7,000,000 cu. ft. of hydrogen is consumed. The feed stock to the desulfurizer contains about 3.5% sulfur. A liquid feed rate of about 1.0 volume per volume of catalyst per hour is employed.

The catalyst is a cobalt molybdate type catalyst consisting essentially of 2% by weight of CoO and 10% by weight of MoO<sub>3</sub> supported on 5% SiO<sub>2</sub>-95% Al<sub>2</sub>O<sub>3</sub>, the carrier in coprecipitated form. The dried SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> cogel is impregnated first with an ammoniacal ammonium molybdate solution, dried, heated to 1200° F. for 2 hours, impregnated secondly with an aqueous solution of cobalt nitrate, dried and heated to 1200° F. for 2 hours.

The off-gas from the desulfurizer contains about 31% hydrogen and about 900,000 cu. ft. per day are bled from the system to prevent build-up of inerts and are processed to recover about 280,000 cu. ft. of hydrogen per day. The fractionated desulfurized product yields 4300 B./D. of diesel fuel.

The 5000 B./D. of 400° F. end point desulfurized gasoline from the desulfurizer are combined with 5000 B./D. of straight run gasoline of 400° F. end point quality and supplied to the reformer operating at about 950° F. and at a pressure of 750 p. s. i. Recycle hydrogen in the amount of about 4000 cu. ft. per barrel is supplied. A feed rate of about 2.5 volumes of charge per volume of catalyst per hour is employed in the reformer.

The reforming catalyst is prepared by sulfiding

a chloroplatinic acid solution and mixing the resulting solution with an aqueous mixture of aluminum fluoride and ammonia. The precipitate is filtered and washed with dilute ammonia and dried. After heating to 1200° F., the catalyst contains about 0.4% by weight of platinum and 4% by weight of halogens.

The reformer feed stock contains about 0.5% sulfur and the product contains 0.001% sulfur. The product from the reformer amounts to about 9260 B./D. The net make gas from the reformer contains about 86.2% hydrogen and amounts to 7,780,000 cu. ft. per day. The make gas is processed to recover the hydrogen which is supplied to the desulfurization reactor.

Off-gases from the coker and cracker contain 37 tons per day of hydrogen sulfide which is removed by scrubbing with an alkaline reagent and about 44 tons of hydrogen sulfide per day are recovered from the off-gas from the desulfurization unit. Hydrogen could be recovered from these gases also.

It is apparent from the foregoing example of my invention that the entire hydrogen requirements for the desulfurization is met by the processing of make gas from the reforming step by adding straight run gasoline to the reforming step which is simultaneously upgraded. The term "straight-run gasoline" is well understood in the art as meaning any gasoline fraction derived from crude oils by simple distillation, as distinguished from hydrocarbon cracking or reforming operations, whether or not such straight-run gasoline fraction may have been subjected to conventional refining treatments such as acid treating, doctor sweetening, or other desulfurizing treatments.

Attempts to desulfurize the entire crude without inclusion of the coking step lead to excessive hydrogen consumption and prohibitive quantities of straight run gasoline are then required. In the present invention carbon-rich material is removed during the coking step with a consequent increase in the hydrogen to carbon ratio of the coker distillate. The amounts of hydrogen required to desulfurize and hydrogenate coker distillate is much lower than that required to process the crude itself. Furthermore, a considerable amount of thermal desulfurization takes place during coking to form hydrogen sulfide thereby decreasing the desulfurization load.

The liquid yield obtained in the three main steps is high and is usually about 80-90 volume per cent for coking, 90-105 volume per cent for desulfurization and 80-95 volume per cent for reforming. The overall yield of marketable liquid products based upon the crude is usually in the range of about 80 volume per cent. In addition a substantial yield of coke and fuel gas is also obtained.

While hypersorption is the preferred method for effecting hydrogen recovery, other separation methods such as low temperature distillation, oil absorption and the like may be employed.

In a hypersorption unit the charcoal must absorb the heavier constituent and transport them downwardly through the adsorption and rectification zones. Hence the greater the concentration of the heavier constituent the greater the charcoal requirement. In the present invention the hydrogen-rich gas produced in the reformer is usually 80-90 volume per cent hydrogen and only a small amount of inerts need be removed therefrom. The off-gas from the desulfurizer usually contains between about 20-50 volume per cent hydrogen. It has been found that the handling of both hydrogen streams in a single hyper-

sorber offers certain advantages in that the heavier constituents are diluted and the amount of rectification is decreased while neither the absorption nor the charcoal recirculation rate need be increased for a given purity of hydrogen production.

Cobalt molybdate is the preferred catalyst for the desulfurization reaction since it has been found that it gives a maximum upgrading of the stock for a minimum hydrogen consumption when it is used under the preferred operating conditions. Other catalysts are less efficient for sulfur removal and especially for nitrogen removal, both of which elements are harmful in that they poison the reforming and especially the platinum catalysts. Olefins are mostly hydrogenated which minimizes carbon formation during reforming. Furthermore, other catalysts consume larger amounts of hydrogen in destructive hydrogenation to form methane, ethane and the like from which the hydrogen is not readily regenerable.

Platinum is the preferred catalyst for the reforming since it is very selective in its dehydrogenation and gives high hydrogen yields of high purity. Other catalysts give less hydrogen. While platinum is generally poisoned by processing even hydrogenated stocks, it has been found that when employed with cobalt molybdate, the removal of oxygen, nitrogen, sulfur, unsaturates, etc., is sufficiently good that platinum catalysts can be operated satisfactorily.

However, where it is desired to employ other catalysts in this invention, it has been found that molybdenum oxides and sulfides, tungsten oxides and sulfides, chromium oxides, vanadium oxides and sulfides and combinations of these elements with themselves or with such elements as copper, cobalt, iron, nickel and the like may be employed either supported or unsupported.

Where very large amounts of straight run gasoline are available for reforming, any of the aforementioned alternative desulfurization catalysts may be employed in the reforming step. Chromium-containing catalysts are particularly useful for this purpose.

The alternative catalysts for desulfurization and reforming are employed in substantially the same reaction conditions as that described hereinbefore for cobalt molybdate and platinum.

The foregoing disclosure of my invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. In a two-stage process for refining hydrocarbons which includes passing said hydrocarbons in admixture with hydrogen into a catalytic hydrodesulfurization zone, withdrawing products from said hydrodesulfurization zone comprising hydrogen and hydrocarbons, separating a first hydrogen-rich gas from said products, recycling at least a part of said first hydrogen-rich gas to said hydrodesulfurization zone, separating a normally liquid desulfurized gasoline stock from said products, passing said gasoline stock in admixture with hydrogen into a catalytic hydroforming zone, withdrawing products from said hydroforming zone comprising hydrogen and reformed gasoline, separating a second hydrogen-rich gas from said products of said hydroforming zone, recycling a first part of said second hydrogen-rich gas to said hydroforming zone, and passing a second recycle

stream of said hydrogen-rich gas to said hydrodesulfurization zone, the improvement which comprises maintaining an endogenous hydrogen balance within said process by mixing with said desulfurized gasoline stock supplied to said hydroforming zone a proportion of a straight-run gasoline stock controlled to provide a net production of hydrogen in said hydroforming zone substantially equal to the consumption of hydrogen in said hydrodesulfurization zone, and passing said net production of hydrogen to said hydrodesulfurization zone.

2. A process according to claim 1 wherein a cobalt molybdate type desulfurization catalyst is employed in said hydrodesulfurization zone and a platinum containing reforming catalyst is employed in said hydroforming zone.

3. A process according to claim 2 wherein said hydrodesulfurization zone is maintained at a temperature between about 750° F. and 850° F. and said hydroforming zone is maintained at a temperature between about 900° F. and 1000° F.

4. In a two-stage process for refining hydrocarbons which includes passing said hydrocarbons in admixture with hydrogen into a catalytic hydrodesulfurization zone, withdrawing products from said hydrodesulfurization zone comprising hydrogen and hydrocarbons, separating a first hydrogen-rich gas from said products, separating a normally liquid desulfurized gasoline stock from said products, passing said desulfurized gasoline stock in admixture with hydrogen into a catalytic hydroforming zone, withdrawing products from said hydroforming zone comprising hydrogen and reformed gasoline, and separating a second hydrogen-rich gas from said products of said hydroforming zone, the improvement which comprises maintaining an endogenous hydrogen balance within said process by including with said desulfurized gasoline stock supplied to said hydroforming zone a proportion of a straight run gasoline stock controlled to provide a net production of hydrogen in said hydroforming zone which is at least equal to the consumption of hydrogen in said hydrodesulfurization zone, recycling at least sufficient of said second hydrogen-rich gas to said hydrodesulfurization zone to balance the consumption of hydrogen therein, and recycling sufficient of said first and second hydrogen-rich gases to said hydrodesulfurization and hydroforming zones to supply the total hydrogen requirements for each of said zones.

5. A process according to claim 4 wherein a cobalt molybdate type desulfurization catalyst is employed in said hydrodesulfurization zone and a platinum-containing reforming catalyst is employed in said hydroforming zone.

6. A process for refining crude oil which comprises passing said crude oil into a coking zone maintained at a temperature between about 800° F. and 1000° F. wherein said crude oil is converted to coke, gases, and a coker distillate having an increased ratio of hydrogen to carbon, separating said coker distillate, passing said coker distillate in admixture with hydrogen into a catalytic hydrodesulfurization zone, withdrawing products from said hydrodesulfurization zone comprising hydrogen and hydrocarbons, separating a first hydrogen-rich gas from said products, recycling at least a part of said first hydrogen-rich gas to said hydrodesulfurization zone, separating a normally liquid desulfurized gasoline stock from said products, passing said desulfurized gasoline stock in admixture with

hydrogen and a straight run gasoline into a catalytic hydroforming zone, withdrawing products from said hydroforming zone comprising hydrogen and reformed gasoline, separating a second hydrogen-rich gas from said products of said hydroforming zone, and recycling a part of said second hydrogen-rich gas to said hydroforming zone, the proportion of straight run gasoline admitted to said hydroforming zone being controlled so that there is a net production of hydrogen in said hydroforming zone which substantially balances the consumption of hydrogen in said hydrodesulfurization zone; and passing said net production of hydrogen to said hydrodesulfurization zone.

7. A process according to claim 6 wherein a cobalt molybdate type desulfurization catalyst is employed in said hydrodesulfurization zone and a platinum containing reforming catalyst is employed in said hydroforming zone.

8. A process according to claim 7 wherein said hydrodesulfurization zone is maintained at a temperature between about 750° F. and 850° F. and said hydroforming zone is maintained at a temperature between about 900° F. and 1000° F.

9. A process for refining crude oil which comprises passing said crude oil into a coking zone maintained at a temperature between about 800° F. and 1000° F. wherein said crude oil is converted to coke, gases, and a coker distillate having an increased ratio of hydrogen to carbon, separating a lower boiling fraction and a higher boiling fraction from said coker distillate, passing said higher boiling fraction through a cracking zone, withdrawing cracked products from said cracking zone, separating from said cracked products a lower boiling fraction and a higher boiling fraction, passing said lower boiling fraction from said coker distillate and said lower boiling fraction from said cracked products in admixture with hydrogen into a catalytic hydrodesulfurization zone, withdrawing products from said hydrodesulfurization zone comprising hydrogen and hydrocarbons, separating a first hydrogen-rich gas from said products, recycling at least a part of said first hydrogen-rich gas to said hydrodesulfurization zone, separating a normally liquid desulfurized gasoline stock from said products, passing said desulfurized gasoline stock in admixture with hydrogen and a straight run gasoline into a catalytic hydroforming zone, withdrawing products from said hydroforming zone comprising hydrogen and reformed gasoline, separating a second hydrogen-rich gas from said products of said hydroforming zone, and recycling a part of said second hydrogen-rich gas to said hydroforming zone, the proportion of straight run gasoline admitted to said hydroforming zone being controlled so that there is a net production of hydrogen in said hydroforming zone which substantially balances the consumption of hydrogen in said hydrodesulfurization zone; and passing said net production of hydrogen to said hydrodesulfurization zone.

10. A process according to claim 9 wherein a cobalt molybdate type desulfurization catalyst is employed in said hydrodesulfurization zone and a platinum containing reforming catalyst is employed in said hydroforming zone.

11. A process according to claim 10 wherein said hydrodesulfurization zone is maintained at a temperature between about 750° F. and 850° F. and said hydroforming zone is maintained at a temperature between about 900° F. and 1000° F.

12. A process according to claim 11 wherein



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the liquid remaining after said separating of a normally liquid desulfurized gasoline stock from said products of said hydrodesulfurization zone is recycled to said cracking zone.

13. A process according to claim 11 wherein the gases produced during coking and during cracking are processed to recover hydrogen and at least a part of said hydrogen is passed into said hydrodesulfurization zone.

14. A process for refining crude oil which comprises passing said crude oil into a coking zone maintained at a temperature between about 800° F. and 1000° F., wherein said crude oil is converted to coke, gases, and a coker distillate having an increased ratio of hydrogen to carbon, separating a lower boiling fraction and a higher boiling fraction from said coker distillate, passing said higher boiling fraction through a cracking zone, withdrawing cracked products from said cracking zone, separating from said cracked products a lower boiling fraction and a higher boiling fraction, passing said lower boiling fraction from said coker distillate and said lower boiling fraction from said cracked products in admixture with hydrogen into a catalytic hydrodesulfurization zone, withdrawing products from said hydrodesulfurization zone comprising hydrogen and hydrocarbons, separating a first hydrogen-rich gas from said products, separating a normally liquid desulfurized gasoline stock from said products, passing said desulfurized gasoline stock in admixture with hydrogen and a straight run gasoline into a catalytic hydroforming zone, withdrawing products from said hydroforming zone comprising hydrogen and reformed gasoline, separating a second hydrogen-rich gas from said products of said hydroforming zone, passing at least a part of said first hydrogen-rich gas into an adsorption zone, adsorbing the more readily adsorbable constituents from said hydrogen-rich gas in constituents from said hydrogen enriched hydrogen from said adsorption zone, recycling a first part of said enriched hydrogen to said hydrodesulfurization zone and passing a second part of said enriched hydrogen to said hydroforming zone, the proportion of straight run gasoline admitted to said hydroforming zone being controlled so that there is a net production of hydrogen in said hydroforming zone which substantially balances the consumption of hydrogen in said hydrodesulfurization zone; and passing said net production of hydrogen to said hydrodesulfurization zone.

15. A process according to claim 14 wherein the gases produced during coking and during cracking are processed to recover hydrogen and at least a part of said hydrogen is passed into said hydrodesulfurization zone.

16. A process for refining crude oil which com-

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prises passing said crude oil into a coking zone maintained at a temperature between about 800° F. and 1000° F. wherein said crude oil is converted to coke, gases, and a coker distillate having an increased ratio of hydrogen to carbon, separating a lower boiling fraction and a higher boiling fraction from said coker distillate, passing said higher boiling fraction through a cracking zone, withdrawing cracked products from said cracking zone, separating from said cracked products a lower boiling fraction and a higher boiling fraction, passing said lower boiling fraction from said coker distillate and said lower boiling fraction from said cracked products in admixture with hydrogen into a catalytic hydrodesulfurization zone, withdrawing products from said hydrodesulfurization zone comprising hydrogen and hydrocarbons, separating a first hydrogen-rich gas from said products, separating a normally liquid desulfurized gasoline stock from said products, passing said desulfurized gasoline stock in admixture with hydrogen and a straight run gasoline into a catalytic hydroforming zone, withdrawing products from said hydroforming zone comprising hydrogen and reformed gasoline, separating a second hydrogen-rich gas from said products of said hydroforming zone, passing at least a part of said first hydrogen-rich gas and said second hydrogen-rich gas into an adsorption zone, adsorbing the more readily adsorbable constituents from said hydrogen-rich gases in said adsorption zone, removing enriched hydrogen from said adsorption zone, recycling a first part of said enriched hydrogen to said hydrodesulfurization zone and recycling a second part of said enriched hydrogen to said hydroforming zone, the proportion of straight run gasoline admitted to said hydroforming zone being controlled so that there is a net production of hydrogen in said hydroforming zone which substantially balances the consumption of hydrogen in said hydrodesulfurization zone; and passing said net production of hydrogen to said hydrodesulfurization zone.

17. A process according to claim 16 wherein the gases produced during coking and during cracking are processed to recover hydrogen and at least a part of said hydrogen is passed into said hydrodesulfurization zone.

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