

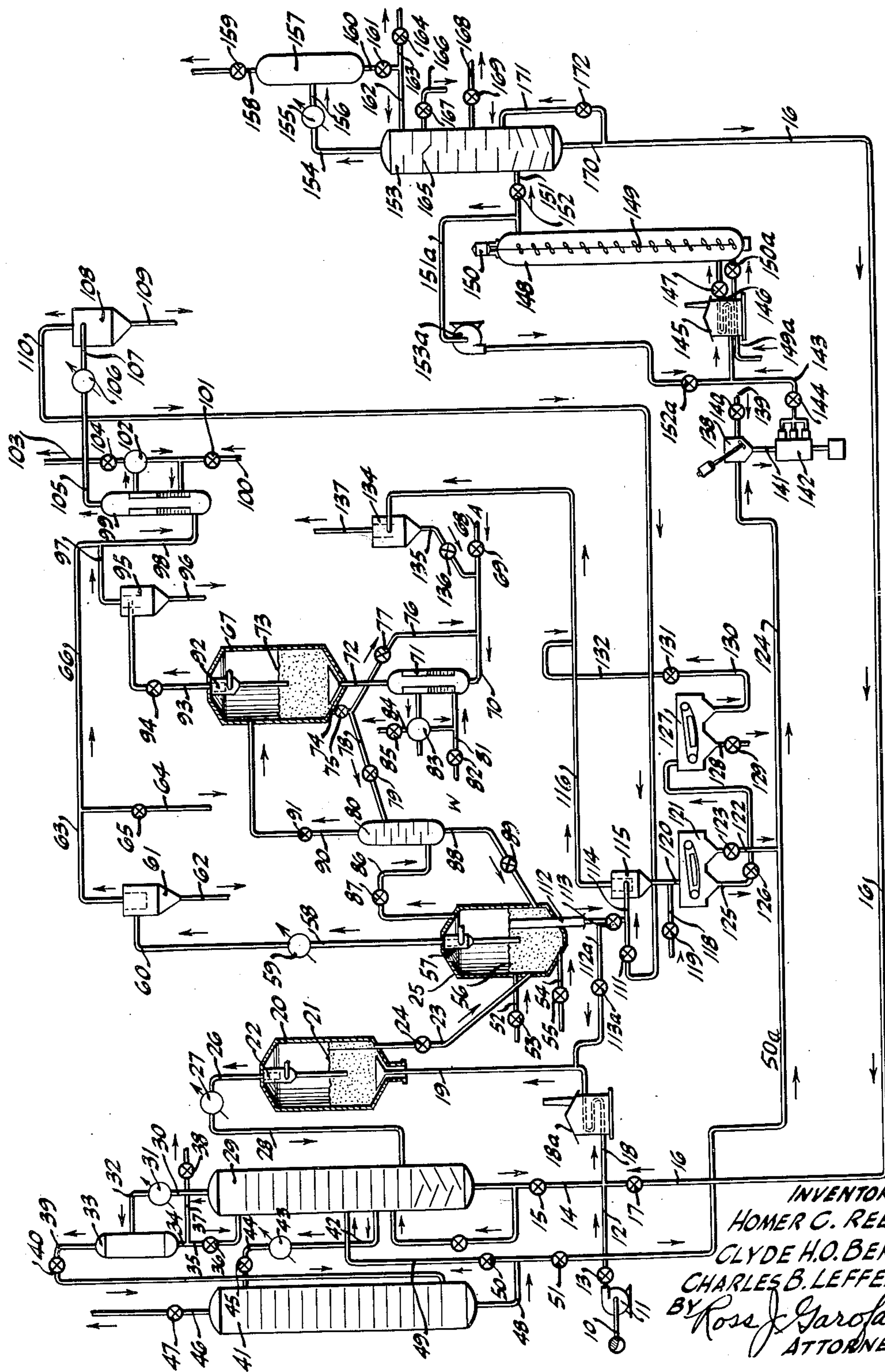
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H. C. REED ET AL

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REFINING PROCESS AND APPARATUS

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INVENTORS.

HOMER C. REED

Clyde H. Berg

CHARLES B. LEFFERT

BY *Rose J. Garofalo*
ATTORNEY.

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REFINING PROCESS AND APPARATUS

Homer C. Reed, Glendale, Clyde H. O. Berg and
Charles B. Leffert, Long Beach, Calif., assignors
to Union Oil Company of California, Los An-
geles, Calif., a corporation of California

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This invention relates to a process and apparatus for the refining of heavy oils such as crude petroleum, straight run and cracked residuums, coker distillates, mineral oils such as those recovered from shale, tar sand, diatomite, and miscellaneous bituminous sands which may or may not be contaminated with undesirable elements such as nitrogen, oxygen and sulfur-containing hydrocarbon compounds, coal oil fractions, particularly those of high density recovered from the distillate produced during coal coking which may be contaminated with acid or basically reacting constituents, for the production of lighter products such as liquids boiling below about 800° F., fractions of which are suitable for fuels in internal combustion engines and diesel engines, lubricating oils, solvents, miscellaneous naphthas, and the like.

More particularly this invention relates to refining processes for the conversion of high density or low A. P. I. gravity oils to products of lower boiling range and lower density which involve coking these oils to form coke and a coker distillate and hydrogenating the distillate in the presence of water, and a metal capable of reacting with water to form hydrogen.

The hydrogenation of mineral oils, and the like, is well known in the art. Generally this has been accomplished by subjecting the oil to be hydrogenated to temperatures of from 200° F. to about 600° F. and from about 1 atmosphere to as high as about 100 atmospheres of hydrogen in the presence of a hydrogenation catalyst usually comprising one of the noble metals such as platinum or palladium, or oxides thereof. The principal disadvantages of such processes include expensive and complex hydrogenation equipment, extensive compression facilities for raising the hydrogen pressure to the level required by the process, expensive, sensitive and easily poisoned catalysts which must be employed, and the problem of catalyst recovery.

It is an object of this invention to provide an easily controlled and efficient process for the hydrogenation of heavy oils for the production of lower boiling fractions.

Another object of this invention is to provide a process for converting high density oils which may be contaminated with undesirable constituents to desirable products of lower boiling range and density including the steps of coking the high density oil in the presence of spent solids from the hydrogenation operation, simultaneously regenerating the spent solids and converting the coke to producer gas and employing the re-

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generated solids in the production of hydrogen and the simultaneous hydrogenation of the heavy oil.

Another object of this invention is to provide an improved process for the recovery of elemental sulfur from sulfur contaminated crude petroleum.

A further object of this invention is to provide an improved process for the reduction of oxides of metals such as iron to lower oxidation states or to their elemental form which involves steps of laying down a layer of coke on the oxide particle and reacting the coke-laden oxide at elevated temperatures in a fluidized vessel to produce producer gas and the metal in a finely divided state.

Another object of this invention is to provide an improved method for the hydrogenation of heavy oils which comprises reacting a finely divided metal or oxide of a metal above hydrogen in the electromotive series of metals with water in the presence of the oil to be hydrogenated to form the metal oxide, recovering the metal oxide from the hydrogenated material, laying down a layer of coke on the oxide particles and converting the coke-bearing oxide to the elemental metal or to a lower oxide for reuse as a hydrogenation catalyst and as a source of hydrogen.

A further object of this invention is to provide an improved continuous process for the hydrogenation of oils with hydrogen produced by the reaction of elemental iron with water or water vapor.

It is also an object of the present invention to provide an apparatus by which the aforementioned processes may be effected.

Other objects and advantages of this invention will become apparent to those skilled in the art as the description thereof proceeds.

Briefly, the preferred modification of this invention comprises the high temperature pyrolysis of hydrocarbon oils in the presence of particles of a spent metal oxide in a fluidized coking zone whereby a layer of coke is laid down on the particles and lower boiling hydrocarbon pyrolysis products are formed, separating the coke-laden oxide particles from the pyrolysis products, reacting the coke with the spent oxide particles in a fluidized reducing regenerating zone to form regenerated particles, combining a portion of the regenerated particles with at least a part of the pyrolysis product, subjecting the mixture thus formed to conditions of superatmospheric temperature and pressure in the presence of water

thereby hydrogenating the pyrolysis product and forming a spent metal oxide, separating desirable fractions of the hydrogenated product thus formed, recovering the spent oxide and recycling it with the high density oil to be coked.

The process of the present invention eliminates virtually all of the aforementioned disadvantages and employs an inexpensive rugged catalyst. The process further utilizes hydrogen generated under superatmospheric pressure in the presence of the oil to be hydrogenated thereby eliminating the compression facilities usually required for high pressure hydrogenations. The hydrogen is generated from water and a metal or a metal compound which also acts as a catalyst. The solids employed are readily recoverable if desired, and such small losses as do occur are not important since the material is readily and inexpensively obtained.

In the process of this invention, the solids employed preferably comprise a finely divided metal above hydrogen in the electromotive series of metals, which may or may not contain a minor quantity of oxides or sulfides of that metal, and which is also capable of reacting with water for the liberation of hydrogen. Such metals as iron, zinc, cobalt, nickel, and the like, may be employed, those of atomic number from 25 to 30 being suitable with exception of copper as well as the lower oxides of these metals. In the preferred modification of the process, finely divided iron of the type generally known as sponge iron, is preferred. These materials are rugged, easily recovered, highly reactive under the conditions of the process, and relatively inexpensive. The iron particles may be prepared in a variety of manners, although the preferred method involves the reduction of finely divided iron oxides known as mill scale obtainable from such sources as rolling mills and the like. The solid particles may also be prepared by the reduction of finely ground and naturally-occurring iron oxides or from other sources.

In the coker, reducing regenerator, and the oxidizing regenerator, "fluidized" suspensions of solids are established in gaseous mixtures in a condition of hindered settling. The gases move upwardly while the solids slowly settle and a thorough countercurrent contact is effected as well as precise temperature control. The iron serves to decompose water to produce the required hydrogen and also perform as a mild hydrogenation catalyst.

During the hydrogenation step of the combination process of this invention, the sponge iron catalyst is commingled with the oil to be hydrogenated and a predetermined quantity of water to form a slurry. This slurry is introduced at high pressures through a heater into an agitated hydrogenation vessel. A completely liquid phase reaction occurs at temperatures sufficiently high to effect the reaction of water and elemental iron and which may be as high as to cause further decomposition of the hydrocarbon to be hydrogenated. By carefully controlling the temperature of the hydrogenation, a variable degree of destructive hydrogenation or combined hydrogenation and cracking may be effected in the presence of iron which may also act as a hydrogenation catalyst as well as the source of hydrogen. During this hydrogenation reaction, the iron is converted to iron oxide. Hydrogenated oil, iron oxide, and unreacted water etc. are introduced into a suitable separating device for recovery of the individual fractions of the mix-

ture. Such a separation may be effected in a conventional fractionating column of the bubble tray type in which hydrocarbon fractions of any desired boiling range may be recovered along with the iron oxide and any residual oil. In such a system, the residual oil contains iron oxide formed in the hydrogenation vessel and this residual fraction is preferably combined with the high density oil to be treated and reprocessed.

Occurring simultaneously with the hydrocarbon hydrogenation step is an efficient desulfurization by means of which sulfur compounds are decomposed with the ultimate formation of iron sulfides which are removed with the iron oxides in the residual oil from the hydrogenation product fractionator. The process provides means for separation of iron sulfides from the iron oxides and the oxidation of such sulfides to form sulfur dioxide. The sulfur dioxide is subsequently converted to elemental sulfur by effecting a reaction of sulfur dioxide with carbon monoxide contained in producer gas. The sulfur may be recovered either as a finely divided solid or as a liquid depending on the temperature. If desirable, this sulfur dioxide may be further oxidized and converted to sulfuric acid.

The nitrogen compounds which may be present in certain types of high density oils to be treated are decomposed under conditions of hydrogenation with the formation of ammonia. Since the hydrogenation is accomplished in the presence of water, the fractionator may be operated under such conditions so that the overhead temperature permits the removal of an aqueous phase containing dissolved ammonia from the upper portion of the column.

The process and apparatus of the present invention may be more clearly understood by reference to the drawing in which a schematic flow diagram of this invention is shown. To further facilitate the description and to also provide a practical operating example of the process, the following description of the drawing will be conducted in the form of an example in which high density crude petroleum produced from the oil fields of Santa Maria Valley (California) is the oil to be treated and in which the catalyst employed is sponge iron. Flow quantities are given and operable ranges of pressure and temperature as well as preferred operating pressures and temperatures are included.

Heavy oil coking

Referring now more particularly to the drawing, 260 barrels per day (42 U. S. gallons per barrel) of Santa Maria (California) crude petroleum amounting to 43.9 tons per day is treated according to the process of this invention. This heavy oil is preferably topped for straight-run gasoline recovery. The crude petroleum passes via line 10 under pressure exerted by pump 11 through line 12 controlled by valve 13 and is combined with 49 barrels per day of coker residuum recycled through line 14 controlled by valve 15 and with a stream containing 8 tons per day of hydrogenated residuum, 2.76 tons per day of iron sulfide, and 20.9 tons per day of ferric oxide flowing through line 16 controlled by valve 17. The combined stream is introduced via line 18 into heater 18a wherein it is heated to a temperature of from about 700° F. to as high as about 1200° F. and preferably to about 900° F. The heated stream

then passes via line 19 into coker 20 wherein pyrolysis of the hydrocarbons is effected with the formation of hydrocarbon pyrolysis products of lower boiling range and a mixture of iron oxide and iron sulfide particles laden with coke.

Coker 20 is a vessel in which the particles of iron compounds such as higher oxides Fe_3O_4 and Fe_2O_3 are maintained in a fluidized state due to the mixing action of hydrocarbon liquid and vapor being introduced from heater 18a. The coke-laden iron compound particles are present in vessel 20 in a state of hindered settling and act much as a high density fluid which accumulates in a lower portion of the vessel. Thus a level 21 exists below which the coke-laden particles are in rapid motion, hindered from settling, and above which the particles tend to settle forming a solid-free gas space. Present within coker 20 is separator 22 by means of which particles of suspended iron compound are removed from the hydrocarbon pyrolysis product and returned to the lower portion of the vessel. Coker 20 preferably is operated at superatmospheric pressure from about zero to as high as 200 pounds per square inch gauge, and preferably between about 30 and 100 pounds per square inch. Coke-laden particles of iron oxide and iron sulfide are removed from coker 20 by means of line 23 controlled by valve 24 and are sent thereby to reducer 25.

The hydrocarbon pyrolysis products, as a vapor phase, pass from separator 22 by means of line 26 through cooler 27 and subsequently via line 28 into coker bubble tower 29 wherein they are fractionated. Other forms of distillation column such as a packed tower may be used as well. The overhead product passes by means of line 30 into cooler 31 wherein a partial condensation of the lower boiling hydrocarbons is effected. The combined liquid and gas pass via line 32 into separator 33 wherefrom the liquid products are withdrawn via line 34. A portion of this passes by means of line 35 controlled by valve 36 into the upper portion of fractionator 29 as reflux while the remaining portion passes via line 37 controlled by valve 38 to further processing facilities or storage facilities not shown. This hydrocarbon stream comprises a coker gasoline which, depending upon the operation of coker bubble tower 29, may have an end point of from as low as about 150° F. to as high as 400° F. In this operation 23.6 barrels per day, or 2.65 tons per day of a 250° F. end point gasoline are produced.

The gas phase present in separator 33 is removed therefrom via line 39 controlled by valve 40 and is introduced into absorber 41 in which the removal of normally liquid hydrocarbon fractions from the gas is effected. To effect this removal, a gas oil fraction is removed from bubble tower 29 by means of line 42, passed through cooler 43 and introduced into absorber 41 by means of line 44 controlled by valve 45. This hydrocarbon fraction, a coker gas oil, passes downwardly through absorber 41 countercurrent to the upwardly rising gases and a dry gas consisting substantially of hydrogen, methane, ethylene, ethane, and the like, is removed by means of line 46 controlled by valve 47.

The rich absorption oil produced in absorber 41 is removed therefrom by means of line 48 a portion of which is returned via line 49 controlled by valve 50 to coker bubble tower 29 while the remaining portion passes by means of line 50a controlled by valve 51 to be hydrogenated as hereinafter described. The quantity of coker distillate

thus produced for hydrogenation amounts to 21.2 barrels per day, or 3.24 tons per day.

Metal oxide reduction

Returning now to the treatment of the coke-laden iron oxides and iron sulfides which are formed in coker 20, these solid particles are collected in one portion of coker 20 from which they are removed by means of line 23 controlled by valve 24 at a rate of 31.4 tons per day and introduced into reducer 25. This solid material analyzes, in per cent by weight, as follows:

Constituent:	Weight per cent
Iron sulfide	8.8
Higher iron oxides	66.4
Coke	22.0
Chloride	1.9
Sulfur	0.9
Total	100.0

This material passes into the reducer at about 900° F.

The operation of the reducer is such that an effective carbon or coke burn-off from the solid particles upon which the coke was laid down in coker 20 is effected. The coke is burned in the presence of an oxygen-containing gas such as air to produce mainly carbon monoxide. This coke burn-off is carried off at temperatures between about 1400° F. and 1800° F. or higher. A suitable temperature for this reaction is about 1650° F. Simultaneously with the coke burn-off, the coke present on the iron oxide particles effects a substantially complete reduction of this iron oxide to an iron compound of a lower oxidation state capable of reacting with water to liberate hydrogen such as particles of ferrous oxide (FeO) or particles of elemental iron in finely divided form. To effect this operation 1.95 MSCF/Hr. (1,000 standard cubic feet per hour) of absorber dry gas or other hydrocarbon gas such as natural gas, which may be preheated to a temperature of about 1200° F., is introduced into reducer 25 via line 52 controlled by valve 53. At these temperatures, a hydrocarbon-iron oxide reaction occurs which gives rise to the formation of carbon monoxide, hydrogen, water and elemental iron. To effect the coke burn-off, 3.81 MSCF/Hr. of air as the oxygen-containing gas, which also may be preheated to a temperature of about 1200° F., is introduced into the lower portion of reducer 25 via line 54 controlled by valve 55. By controlling the operation of reducer 25, the contents of the vessel are maintained in such a condition that the solid particles are hindered from settling and a suspension of the solid particles having level 56 is maintained in the lower part of the vessel.

Above level 56 is collected a producer gas rich in carbon monoxide and hydrogen which is formed during the iron oxide reduction. To produce high purity iron from the reducer, it is preferable to maintain a carbon monoxide to carbon dioxide ratio (volume) of greater than about 1.0 in the producer gas such as between about 2.5 and 5.0. A ratio of about 3.0 is preferred to insure reduction of the oxides to elemental iron. For reduction to ferrous oxide (FeO), a ratio of from about 0.5 to as high as about 3.0 may be used. This gas is introduced into separator 57 in which traces of suspended particles are removed and returned to the high density sus-

pension phase below level 56. From the upper portion of separator 57, 5.39 MSCF/Hr. of a producer gas analyzing about 80% carbon monoxide is removed at a temperature of about 1650° F. via line 58. This producer gas passes subsequently through heat exchange means 59 whereby it is cooled considerably losing its heat, in one modification of this invention, in indirect heat exchange with the hydrocarbon gas and air introduced, as previously described, into reducer 25. The producer gas is thus cooled to a temperature below 1,000° F. and is passed by means of line 60 into separator 61 wherein remaining traces of suspended solid particles are removed. These particles may be recovered from the producer gas in a high voltage electrical precipitator or in a specially designed centrifugal type separator such as a cyclone. Recovered particles may be returned to reducer 25 via line 62. The solids-free producer gas is removed from separator 61 by means of line 63 and a portion of this is sent via line 64 controlled by valve 65 for use as fuel, such as in furnace 13a in which the incoming heavy oil feed, recycle coker residuum, and hydrogenated residuum are raised to coking temperatures prior to their introduction into coker 20. The remainder of the carbon monoxide gases pass via line 66 for further processing in connection with the recovery of elemental sulfur from the sulfur dioxide bearing gases produced during the conversion of iron sulfide to iron oxide, as hereinafter more fully described. The reduced solids are removed from reducer 25 via line 112 and a portion may be passed through line 112a controlled by valve 113a directly into the coker in which part of the desulfurization may be effected at coking temperatures.

Metal sulfide oxidation

In oxidizer 67, 7.73 tons per day of solid material containing 91% iron sulfide, magnetically separated from the reducing regenerator effluent, as hereinafter described, are introduced and converted to higher iron oxides. This reaction is conducted at a temperature of about 1200° F. although temperatures as low as about 1,000° F. to as high as about 2,000° F. or higher may be employed, if desired. The iron sulfide is suspended in an air stream introduced by means of line 68 controlled by valve 69 and the suspension together with recirculated iron oxide is passed via line 70 through waste heat boiler 71 wherein a portion of the heat generated during oxidation of the iron sulfide is dissipated in converting water introduced via line 81 controlled by valve 82 into steam which is removed from separator 83 via line 84 controlled by valve 85. The suspension is then passed from boiler 71 via line 72 into oxidizer 67. A level 73 is maintained in oxidizer 67 below which iron sulfide and iron oxide particles are maintained in a condition of hindered settling as a relatively high density suspension. The solid particles are removed from oxidizer 67 via line 74 controlled by valve 75 and a portion thereof is returned via line 76 controlled by valve 77 to be recombined with the incoming iron sulfide and air for recirculation through waste heat boiler 71. The quantity of this recycle stream amounts to about 108 tons per day, although higher or lower recycle rates may be employed in order to maintain the oxidizer temperature at the desired value. The remaining quantity of oxidized material passes via line 78 controlled by valve 79 into auxiliary

reducer 80 at the rate of 7.1 tons per day and has approximately the following composition:

Constituent:	Weight per cent
Fe ₂ O ₃ -----	83.0
Fe ₃ O ₄ -----	9.1
FeS -----	7.9
	100.0

Within auxiliary reducer 80 this downwardly flowing solid mixture contacts a countercurrent stream of gas removed from reducer 25 at a rate of 1.4 MSCF/Hr. by means of line 86 controlled by valve 87 and which contains carbon monoxide. This countercurrent contact effects a substantially complete reduction of the Fe₂O₃ to Fe₃O₄, and simultaneously the solids are heated to approximately the temperature existing within the reducer, that is, about 1650° F. The Fe₃O₄ thus produced, containing about 8.0% iron sulfide and substantially no Fe₂O₃, is passed from auxiliary reducer 80 by means of line 88 controlled by valve 89 into reducer 25. The gas removed from auxiliary reducer 80 after contacting the oxidized iron sulfide from oxidizer 67 passes via line 90 controlled by valve 91 into oxidizer 67. Within oxidizer 67 the iron sulfide is oxidized to a mixture of iron oxides with the simultaneous production of gases rich in sulfur dioxide. Under conditions of the present operation these gases are removed from oxidizer 67 through separator 92 by means of which suspended particles of iron oxides are separated and returned to a point below level 73. The solids-free sulfur dioxide bearing gases are removed from separator 92 by means of line 93 controlled by valve 94 and are introduced into separator 95 which preferably is of the high voltage type, by means of which remaining traces of very fine solids are precipitated. The solids thus recovered may be disposed of or returned to the system by means of line 96. The sulfur dioxide bearing gases, free from suspended particles, pass from separator 95 by means of line 97 at a rate of 22.0 MSCF/Hr. and are combined with 14.3 MSCF/Hr. of producer gas containing a high concentration of carbon monoxide flowing through line 66.

Sulfur production

The gaseous mixture thus formed has a temperature of about 1100° F. and contains carbon monoxide and sulfur dioxide under conditions at which they readily react to produce elemental sulfur according to the following reaction:



This gaseous mixture is conducted by means of line 98 into waste heat boiler 99 wherein the heat generated is employed to convert water to steam. Water is introduced by means of line 100 controlled by valve 101 and steam formed is removed from separator 102 by means of line 103 controlled by valve 104. The heat made available by this reaction is about 300,000 B. t. u. per hour, a substantial portion of which is recoverable in the form of high pressure steam. Gases are removed from boiler 99 at a temperature of about 1185° F. by means of line 105 and are introduced into heat exchange means 106 wherein the gases are preferably cooled to a temperature of below about 250° F. losing their heat in this modification at a rate of about 500,000 B. t. u. per hour in the generation of steam. Sulfur is hereby precipitated in solid form and liquid sulfur may be recovered, if

desired, by maintaining the temperature above 250° F. such as for example, at least 300° F. This gas is introduced via line 107 into separator 108 wherein the sulfur is separated. Sulfur is thus produced at a rate of about 1.8 tons per day and is removed from separator 108 via line 109. The sulfur thus produced is of high purity. The solid sulfur is in a finely divided form suitable for a wide variety of uses, especially fruit tree dusting.

The reaction of carbon monoxide and sulfur dioxide does not go to completion so that the gases removed from separator 108 by means of line 110 are contaminated with unreacted quantities of sulfur dioxide and small quantities of hydrogen sulfide formed through the reaction of sulfur dioxide with water vapor. In order to recover these quantities of sulfur, the gas removed from separator 108 via line 110 controlled by valve 111 is employed at a rate of about 34.2 MSCF/Hr. to convey and simultaneously to cool the iron effluent removed from reducer 25 at a rate of 26.2 tons per day by means of line 112 controlled by valve 113. These solids are removed from reducer 25 at a temperature of about 1650° F. and have approximately the following weight composition:

Constituent:	Weight per cent
Iron	4.95
Iron oxide (FeO)	17.0
Iron oxide (Fe ₃ O ₄)	9.9
Iron sulfide	21.3
Chloride	2.3
	100.0

In doing this an efficient contact of the residual sulfur-bearing gases with iron is effected substantially completely converting the sulfur to nonvolatile metal compounds such as iron sulfide. The metal sulfur compounds are recirculated through the system for reprocessing and permit the discharge to the atmosphere of gases substantially uncontaminated with sulfur and a substantially complete sulfur recovery. The gaseous suspension thus formed passes by means of line 114 into separator 115 wherein the solids, comprising a mixture of iron oxide and iron sulfur compounds together with iron, are separated from the heated gases. The solids thus conveyed and cooled are removed from separator 115 at a rate of about 26.7 tons per day at a temperature of about 825° F. These solids have approximately the following composition:

Constituent:	Weight per cent
Iron	45.0
FeO	16.6
Fe ₂ O ₃	9.7
FeS	26.5
Chloride	2.2
	100.0

Gases are removed from separator 115 at a temperature of 825° F. via line 116 having a substantially reduced sulfur content.

The solid material containing recovered iron sulfur compounds removed from separator 115 passes via line 120 and may be quenched by direct contact with about 80 tons per day of water introduced by means of line 118 controlled by valve 119. The temperature is thus reduced to about 150° F. and 190,000 B. t. u. per hour of heat are recovered. The slurry of solids in water passes via line 120 into primary magnetic separator 121.

wherein a substantially complete separation of iron sulfides is effected. The elemental iron and iron oxides thus recovered is removed from separator 121 via line 122 controlled by valve 123 at a rate of 25.1 tons per day. The stream has approximately the following composition:

Constituent:	Weight per cent
Iron	47.9
FeO	17.7
Fe ₃ O ₄	7.8
Chloride	2.4
Water	24.2
	100.0

This slurry of iron and water is combined with 212 barrels per day of coker distillate removed from the lower outlet of absorber 41 and flowing through lines 48 and 50a controlled by valve 51. This material is subsequently passed by means of line 124 to the hydrogenation step of the process which will subsequently be described.

Also removed from magnetic separator 121 is a stream of the relatively nonmagnetic materials containing substantially all of the iron sulfide, and some iron oxide, the chlorides, and the like. This material is removed by means of line 125 controlled by valve 126 and is introduced into secondary magnetic separator 127 wherein a separation of the ash and chlorides is effected from the iron oxides and iron sulfides. The ash and chlorides and other nonmagnetic materials are removed by means of line 128 controlled by valve 129 and are discarded. The iron sulfide concentrate is removed by means of line 130 controlled by valve 131 at a rate of about 10.2 tons per day and has approximately the following composition:

Constituent:	Weight per cent
FeS	69.4
Fe ₃ O ₄	6.4
Water	24.2
	100.0

This material passes by means of line 132 and is combined with a large volume of gases removed from separator 115 via line 116 at a temperature of about 825° F. This gas is again employed to convey solid materials and simultaneously to remove last traces of sulfur compounds. Water is evaporated to form a completely gaseous suspension of iron sulfide and a small quantity of iron oxide (Fe₃O₄) and the suspension is passed by means of line 133 into separator 134 at a temperature of about 425° F. Within separator 134, suspended particles of FeS and Fe₃O₄ are removed from the suspended gas. These are passed by means of line 135 controlled by valve 136 at a rate of 7.7 tons per day to be combined with air for introduction into oxidizer 67. The sulfur-free gases are discharged to the atmosphere by means of line 137 at a rate of about 34 MSCF/Hr. A substantially complete sulfur recovery as elemental sulfur may be effected in this manner.

Hydrogenation

Returning now to the actual hydrogenation step, the coker distillate flowing through line 50 at a 212 barrel per day rate is combined in line 124 with 25.1 tons per day of a slurry of iron and water formed as described above. The slurry passes via line 124 into mixer 138 to which additional water may be added by means of line 139 controlled by valve 140, if desired. With this additional water may be added water-soluble salts

of various types which enhance the hydrogenation reaction or these hydrogenation accelerators may be added, if desired, directly to the hydrogenation reactor. Hydrogenation accelerators applicable in this respect are the water-soluble halides of metals such as calcium, magnesium, iron, manganese, and the like, as well as the halides of ammonia.

The slurry prepared in mixer 138 passes by means of line 144 into high pressure pump 142 by means of which the slurry is compressed to a pressure which approximates that required in the ultimate hydrogenation reaction. This slurry is passed under high pressure through line 143 at a rate of 59.6 tons per day controlled by valve 144 into heater 145. Material introduced into heater 145 has the following weight composition:

Constituent:	Weight per cent
Fe -----	20.1
FeO -----	7.5
Fe ₃ O ₄ -----	3.3
Chloride -----	1.0
Water -----	13.8
Coker distillate -----	54.3
	100.0

In other operations, the composition may be varied to obtain different degrees of hydrogenation. From 5% to 35% iron, or ferrous oxide, 2% to 25% water, and 30% to 90% oil may be employed, for example.

This material is removed from heater 145 by means of line 146 controlled by valve 147 and is introduced at a temperature between about 500° F. and 1200° F. into hydrogenation reactor 148. In this particular operation a temperature of about 750° F. was employed in the hydrogenation of the coker distillate. Hydrogenation reactor 148 is provided with agitator 149 and driving means 150 whereby the contents of the reactor are maintained in a condition of thorough agitation during the entire reaction.

It is sometimes desirable, where heating of the combined hydrogenation reactor feed is not feasible, to separately heat the oil containing the suspended iron in one stream and the water which may contain a dissolved hydrogen generation accelerator in the other. In this modification, the magnetic separation is effected in the absence of water. The water is then introduced at high pressure via line 149a through a separate coil in heater 145 at a rate controlled by valve 150a directly into reactor 148. The temperature may be above or below that of the inlet oil stream and may in some instances be at pressure and temperature conditions above the critical. Such an operation permits the complete iron-steam reaction for hydrogen production to take place under the conditions best suited for hydrogenation. A very effective utilization of the hydrogen thus formed is effected.

The pressure under which the hydrogenation reaction is accomplished is above atmospheric ranging as high as 15,000 pounds per square inch (1,000 atmospheres). Lower pressures may be employed such as less than about 100 pounds per square inch, although in the hydrogenation of such material as coker distillate obtained from Santa Maria Valley crude petroleum, pressures in the range of from 3000 to 9000 pounds per square inch are desirable.

During its passage through hydrogenation reactor 148 the mixture of iron, water and coker distillate reacts for the conversion of the un-

saturated hydrocarbon constituents of the coker distillate to saturated or paraffinic fractions, the destructive hydrogenation of the higher molecular weight and higher boiling hydrocarbon constituents for the production of saturated hydrocarbons boiling in the lower temperature ranges, the destruction of nitrogen, oxygen and sulfur-containing hydrocarbon compounds with the formation of ammonia, water, and hydrogen sulfide, respectively, and substantially completely hydrogenated remnants of these constituents, the conversion of the iron and FeO through reaction with water to higher oxides of iron such as Fe₃O₄ with the simultaneous production of hydrogen which is employed substantially as it is formed in the aforementioned hydrogenation reactions, and the conversion of a portion of the iron or iron oxides to sulfides of iron through reaction with hydrogen sulfide or with the sulfur-containing hydrocarbon compounds.

The heterogeneous mixture of solids and liquids containing dissolved gases is removed from hydrogenation reactor 148 by means of line 151 controlled by valve 152. A portion of the hydrogenation reactor effluent thus removed may be recycled through heater 145 via line 151a controlled by valve 152a by circulation pump 153a. In this manner the entire system, heater and reactor, may operate under substantially isothermal conditions so that hydrogen generated by reacting iron with water is formed at the hydrogenation temperature permitting a substantially complete utilization as formed. Such a mixing of a portion of the hydrogenated effluent with the feed to the reactor permits quick heating and avoids the condition encountered whereby the hydrogen is generated at temperatures during heating which are not sufficiently high to effect the desired degree of hydrogenation.

The remaining portion of the reactor effluent is introduced into the central lower portion of hydrogenation effluent bubble tower 153. In this fractionating column, the hydrogenated effluent is separated into its constituent parts. An overhead vapor passes by means of line 154 into condenser 155 wherein a partial condensation of the lower boiling constituents is effected. This cooled product passes by means of line 156 into separator 157 from which the gases are removed by means of line 158 controlled by valve 159 which also maintains a back pressure on the column. The gas thus obtained may contain a certain amount of hydrogen as well as the normally gaseous hydrocarbon constituents. This gas may be employed as fuel in the process, or may be sent to storage or further processing facilities not shown. The condensate is removed from separator 157 via line 160 controlled by valve 161 and a portion is returned to the upper part of the bubble tower by means of line 162 as reflux, while the remainder is produced through line 163 at a rate of 55 barrels per day controlled by valve 164. This liquid fraction comprises a hydrodesulfurized gasoline which is substantially free from nitrogen and sulfur contamination. The gasoline may be blended in any desirable proportion with unsaturated hydrocarbon fractions obtained from the coker gasoline product produced from the upper portion of coker bubble tower 290, previously described.

The conditions of temperature and pressure which are employed in the hydrogenation step of the process may be modified by the incorporation of catalytic quantities of such hydrogenation and/or desulfurization catalysts as nickel and cobalt oxides or sulfides. Molybdenum or tung-

sten oxides or sulfides may also be employed. To enhance desulfurization, catalysts such as cobalt molybdate, cobalt chromate, and the corresponding nickel compounds may be introduced with the mixture of water, oil, and iron or ferrous oxide into the hydrogenation reactor. The cobalt and nickel oxides and sulfides are especially applicable since these compounds are readily regenerated under the existing conditions of operation in which the oxides of iron are reduced. By employing catalytic quantities of these compounds in the hydrogenation reactor, considerable reductions in temperature and pressure result. Those pressures and temperatures in the lower part of the ranges given above permit good conversions; that is, temperatures between about 700° F. and 800° F. and pressures of less than about 5000 pounds per square inch.

Ammonia is produced during the destructive hydrogenation of nitrogen-containing hydrocarbons. In order to effect an efficient recovery of this compound, the reflux temperature of bubble tower 153 may be maintained at about 210° F. under atmospheric pressure operation whereby a substantially complete recovery of unreacted water containing dissolved ammonia may be effected by continuously drawing off this commodity from tray 165 through line 166 controlled by valve 167. A hydrodesulfurized gas oil having a boiling range of from about 200° F. to about 800° F. may be removed, if desired, from the middle portion of column 153 via line 168 controlled by valve 169. This commodity is produced at a rate of 157 barrels per day.

The bottom part of column 153 is maintained at a temperature of between 700° F. and 1000° F. and a small quantity of hydrogenated residuum is removed via line 170. A portion of this is recycled by means of a pump not shown through line 171 controlled by valve 172 to a point somewhat above the inlet of the material removed from hydrogenator 148. The quantity of this residuum amounts to 49 barrels per day. This material has the following weight composition:

Constituent	Weight per cent
Hydrogenated residuum	24.8
FeS	8.6
Fe ₃ O ₄	64.7
Chlorides	1.9
	100.0

This material is recirculated by means of line 16 from bubble tower 153 to be combined with the Santa Maria Valley crude oil passing with the coker bubble tower residuum via line 18 into heater 18a completing the cycle.

According to the modification of the process of this invention, as above described, an efficient economical and easily controlled process for the substantially complete conversion of high density oils into desirable hydrocarbon fractions of lower density and lower boiling range is provided. Furthermore, the products which are obtained through application of the process are substantially free from undesirable nitrogen, oxygen and sulfur compound contamination and provide highly desirable raw materials for the formulation of internal combustion engine fuels such as gas, gasoline, diesel fuel, and the like, and may also provide suitable stocks for the preparation of high quality lubricating oils and greases.

It is to be understood that although the foregoing description of the process of this invention was one involving specific conditions of tempera-

ture, pressure, composition, etc., these conditions are not to be considered limiting since a certain latitude of variation is permissible whereby the desirable results may be obtained. It is to be further understood that although the high density oil treated in the above description was a high density crude petroleum having an A. P. I. gravity of between 10.0 and 12.0, other high density oils may be similarly treated and the same desirable results effected.

The operation of the reducer may be varied such as by altering the temperature and the carbon monoxide concentration to form ferrous oxide, FeO, in preference to elemental iron. This then may be reacted with water to yield the hydrogen required in the hydrogenation step. The use of ferrous oxide instead of elemental iron has been found to be of advantage, since under some conditions of operation, such as in the higher temperature range, there is no tendency for the ferrous oxide to sinter or agglomerate or otherwise to form larger particles at the expense of the smaller particles and reduce the active surface of the material.

In another modification of the process of this invention, fluidized operations are also performed in the coking of the oil feed in the presence of coker residuum and hydrogenated residuum, in the oxidation of iron sulfide to iron oxide to form sulfur dioxide and in the reduction of iron oxide to iron in which latter step the coke laid down on the iron oxide during the coking operation is removed by combustion with the formation of a gas rich in carbon monoxide similar to the preferred process described above. Herein the oxidizing regenerator may produce sulfur dioxide or elemental sulfur depending on oxidizing conditions.

In this modification the high gravity oil such as crude oil, shale oil, tar sand oil, coal oil, residuums, and the like, is combined with a hydrogenated residuum containing suspended particles of iron sulfide and iron oxide. The stream is then combined with a stream of iron oxide (Fe₃O₄ predominantly) and is passed preferably through a fired heater where the temperature is raised to between about 700° F. and 1200° F. to initiate a thermal pyrolysis. The heated material is then introduced into a fluidized coking vessel. In the coking vessel, thermal pyrolysis of the heated combined oil streams is effected in the presence of suspended particles of iron oxides and iron sulfides. A level is maintained within the coking vessel below which the heated particles of iron oxides and iron sulfides are maintained in a condition of hindered settling wherein the coke resulting from the thermal pyrolysis reaction is deposited on the suspended solid particles. Above this level accumulates the pyrolysis products comprising hydrocarbons in the vapor phase. These hydrocarbons pass through a separator present in the upper portion of the coking vessel wherein small quantities of suspended particles are separated and returned to the lower portion of the coking vessel below the level of solid particles. The solids-free pyrolysis product comprising hydrogen and saturated and unsaturated hydrocarbons having boiling points as high as about 800° F. and higher are removed from the separator and introduced into a coker bubble tower where fractionation of the hydrocarbons thus produced is effected.

In the coker bubble tower an overhead gas product containing hydrogen, methane, saturated and unsaturated C₂ and some C₃ hydrocar-

bons is produced. Condensation of a portion of the vapor removed from the upper portion of the column forms a coker gasoline having a boiling range from about 70° F. to as high as about 400° F. The end point of this coker gasoline may be varied by varying the overhead product temperatures of the coker bubble tower. A coker gas oil may be removed from the coker bubble tower at a point intermediate between the pyrolysis product inlet and the overhead vapor outlet. This product contains saturated and unsaturated hydrocarbons boiling in the range of from about 300° F. to as high as about 800° F., the actual boiling range depending upon variable operating conditions of the column. From the bottom of the coker bubble tower, a coker residuum is removed which may be recirculated and combined with a feed stream and reintroduced into the coking vessel for reprocessing. This residuum may also be employed as a raw material for road-building hydrocarbons such as road oil, asphalt, and the like.

If desired, the coker gasoline and coker gas oil may be combined to form a coker distillate which is hydrogenated for the formation of desulfurized and saturated hydrocarbons suitable for internal combustion and engine fuels, lubricating oils and greases. If desired, these streams may also be treated individually by hydrogenation as will be subsequently described, or by other processes.

Returning now to the coking vessel, a stream is removed from below the level maintained in the coking vessel which comprises coke-laden particles of iron oxide (Fe_3O_4 predominantly), and iron sulfide. This material is suspended in a gas, if desired, or is otherwise directly introduced into a fluidized reducing regenerator.

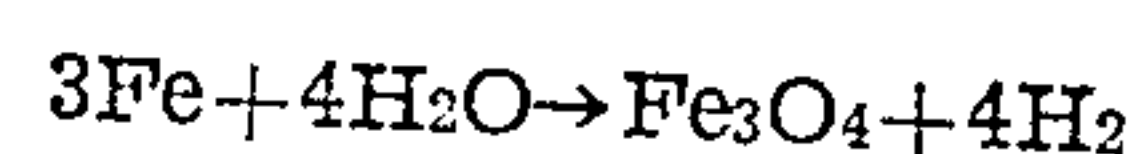
The reducing regenerator effects the combustion of carbonaceous materials such as coke present on the iron oxide and iron sulfide particles, and also effects a substantially complete reduction of the Fe_3O_4 to finely divided elemental iron or to lower iron oxides such as FeO . The temperature of operation at which the reducing regenerator effects these conversions may be between about 1000° F. and 2000° F., a temperature of about 1650° F. being typical. An oxygen-containing gas such as air is introduced directly into the reducing regenerator in controlled quantities to effect coke combustion which favors the formation of carbon monoxide and liberates heat aiding the iron oxide reduction. Introduced at a separate point in the reducing regenerator is a gas containing hydrocarbons and/or carbon monoxide such as natural gas, producer gas, or mixtures and the like, which assists the reduction of oxides of iron to lower oxides or elemental iron. These gases, the oxygen-containing gas, and the producer gas or natural gas are preferably introduced below the level of suspended solids maintained in a fluidized state in the reducing regenerator. It is also to be preferred that a portion of these suspended solids be continuously removed, passed through suitable heat exchange means, and reintroduced in a closed cycle to maintain temperature control of the reaction.

In the reducing regenerator conditions are controlled so that the gases produced during the reaction contain hydrogen and water vapor in a ratio of about 2.0 and carbon monoxide and carbon dioxide in a ratio of at least 3.0. Under a pressure of operation which may range from near atmospheric to as high as several hundred

pounds per square inch and under the conditions of temperatures disclosed above the production of a gas containing the constituents recited in the ratios given insure a substantially complete conversion of coke and of the iron oxide introduced into the reducing regenerator to finely divided elemental iron. A stream consisting of iron and iron sulfide essentially, and also containing small quantities of iron oxide is continuously removed from the reducing regenerator and subjected to a magnetic separation wherein the iron and the other materials with high magnetic susceptibility are separated from the iron sulfide. The iron thus recovered is employed in the hydrogenation of the coker distillate.

The iron sulfide recovered from the magnetic separator is combined with air and continuously introduced into an oxidizing regenerator in which the oxidation of iron sulfide to iron oxide is conducted under conditions suitable for maintaining the solids in a state of hindered settling and at a temperature of from 1000° F. to as high as 2000° F. In the oxidizing regenerator a suspension of solids is maintained in which a level of fluidized solids is present. In the upper portion of the oxidizing regenerator the gases produced in the oxidation reaction are passed through a centrifugal separator for the removal of suspended solid particles. Suspended solids-free gases are subsequently removed from the separator containing sulfur dioxide or elemental sulfur depending upon the conditions of operation. Elemental sulfur in liquid or solid form may be produced in the system by operating with a minimum quantity of air required in the iron sulfide oxidation and by controlling the effluent gas temperature so that at least part of the iron sulfide is converted to iron oxide and sulfur. In this modification the iron oxide formed from the iron sulfide oxidation is continuously removed from the oxidizing regenerator, cooled, and combined with the hydrocarbon feed to be coked and is introduced therewith through the heater into the fluidized coking vessel.

As indicated above, the stream of solids removed from the reducing regenerator is magnetically treated to recover a concentrate of elemental iron. This is mixed to form a slurry with at least part of the hydrocarbons obtained from the coker bubble tower and with water. The actual quantities of iron and water in relation to the amount of oil to be hydrogenated have been set forth above and are dependent upon the quantity of olefinic or otherwise unsaturated hydrocarbons which are desirably converted to paraffinic or saturated compounds. Under the conditions of the hydrogenation, iron reacts with water with the formation of iron oxide and the liberation of hydrogen according to the following reaction.



This reaction supplies hydrogen required in the hydrogenation reaction and is consumed substantially as it is formed. The quantity of iron and water is selected to provide sufficient hydrogen to effect the desired degree of hydrogenation.

It is desirable to assist the hydrogenation reaction and the hydrogen generation by the addition to the slurry of halides of ammonia or various metals such as iron, manganese, magnesium, calcium, and the like, which function as accelerators.

The slurry, containing the constituents above described, is pumped through a means for heat-

ing whereby temperatures from about 500° F. to about 1200° F. or more are developed in the system. The heated oil is introduced thereby into a hydrogenation reactor at a pressure as high as about 15,000 pounds per square inch. This vessel is preferably continuously agitated to permit uniform suspension of the reacting solids in the liquid and to assist temperature control. Water, heated and under pressure, may be added separately from the oil and iron, or the slurry may be combined with a part of the hot reactor effluent and introduced into the reactor.

In the hydrogenation reactor, sulfur-containing hydrocarbon constituents are decomposed presumably by destructive hydrogenation with the formation of hydrogen sulfide and the hydrocarbon remnant of the sulfur compound. The hydrogen sulfide ultimately reacts with either the iron or the iron oxides present forming iron sulfide in the system. Nitrogen-containing hydrocarbon compounds are similarly decomposed forming ammonia. The hydrogenator effluent containing the above indicated constituents is subsequently passed from the hydrogenation reactor to a means for effecting the separation of the various constituents. In the preferred modification this means for separation may comprise a distillation column from which gaseous hydrocarbons are removed together with hydrogenation hydrocarbon fractions, gas oil fractions and others. Provision is preferably made in the distillation column for the removal of water containing dissolved ammonia which may be substantially completely recovered by this means. From the lowest part of the distillation column a hydrogenated residue of higher boiling hydrocarbons is removed which contains suspended solids including iron oxide, iron sulfide, and possibly some unreacted iron. This residuum may be magnetically separated for the recovery of solid particles, or in the preferred modification is combined in its entirety with the heavy oil to be hydrogenated and is returned with that stream to the coking vessel for retreatment.

In accordance with this modification a high density oil is subjected to conditions of thermal pyrolysis and destructive hydrogenation whereby a substantially complete conversion to hydrocarbon fractions to more desirable boiling range is effected. By-products, including ammonia, sulfur dioxide, sulfur, and possibly various sulfides and oxides of iron may be produced, if desired. One outstanding feature of this process is the fact that a high pressure hydrogenation may be effected in the complete absence of the extensive gas compression facilities normally required in high pressure hydrogenation operations and also in the absence of an expensive and often easily poisoned hydrogenation catalyst. Another advantage of this modification comprises the use of the magnetic separating means for the control of iron sulfide by separating this material continuously and converting it by oxidation to iron oxide. This eliminates recycling of iron sulfide uselessly through the process.

In an additional modification of the process according to this invention, a fluidized coker, a fluidized oxidizing regenerator and a fluidized reducing regenerator are also employed. In this particular operation the heavy hydrocarbon stream to be treated is combined with a hydrogenated residuum containing iron oxide and iron sulfide and with a coker residuum and introduced via a fired heater into the coking vessel. The oxidizing regenerator is so positioned with respect

to the coker that iron oxide withdrawn from the oxidizing regenerator is combined with the heated hydrocarbon stream from the heater and the two are introduced simultaneously into the coking vessel. In this manner a substantial utilization of the sensible heat of iron oxide from the oxidizing regenerator is utilized in causing thermal pyrolysis of the heavy oil being coked. Also in this manner iron oxide from the oxidizing regenerator is passed through the coking vessel and a layer of coke is deposited upon each particle. The hydrocarbon stream from the heater may be at a temperature of between about 700° F. and 1200° F. and usually at a temperature of about 950° F. and is combined with iron oxide from the oxidizing regenerator at a temperature of about 1200° F. prior to passing into the coking vessel. This operation may be modified somewhat by introducing the iron oxide directly from the oxidizing regenerator into the coking vessel.

The operation of the coking vessel is that of a fluidized system previously referred to wherein a level of suspended solids is maintained. In the upper portion of the coking vessel is situated a centrifugal separator whereby the pyrolysis products as vapors may be removed from the coker while retaining suspended solid particles in the coking vessel. The pyrolysis product is subsequently introduced into a distillation column which may be of the bubble tray type wherein various hydrocarbon fractions, gaseous and liquid, are separated from one another. During coking, a certain quantity of hydrogen sulfide is generally formed from the decomposition of sulfur-containing hydrocarbon constituents. This material is removed together with the hydrogen, C₁ and C₂ saturated and unsaturated hydrocarbons from the upper portion of the column. In one modification of this invention, the gas thus produced is subjected to a treatment adaptable to removing the hydrogen sulfide thus contained such as by absorption in basically reacting adsorbents such as aqueous solutions of alkali metal salts, absorption in solutions of organic compounds such as ethanalamines, and the like. The hydrogen sulfide-free hydrocarbon gases are introduced into the reducing regenerator to effect the reduction of iron oxide to finely divided metallic iron as subsequently described.

The normally liquid portion of the hydrocarbons in the pyrolysis product are further fractionated in the coker bubble tower to produce a coker distillate or coker gasoline boiling from about 100° F. to 400° F. and a coker gas oil boiling from about 350° F. to about 760° F. These individual fractions may be produced and sent to storage, individually hydrogenated according to the process of this invention, or produced from the bubble tower as a single coker distillate stream the total quantity of which is then hydrogenated.

From the lowest portion of the coker bubble tower is removed a coker residuum consisting of the higher boiling hydrocarbons which may be employed as fuel oil, road oil, in the preparation of asphaltic road-building material, and the like. This residuum in the present invention is preferably combined with the hydrogenated residuum and with the high density oil to be treated and the combined stream is introduced into the coker for pyrolysis.

From the lower portion of the coking vessel is removed a stream of finely divided solids comprising a mixture of iron oxide, iron sulfide and coke. In this modification of the invention a

minor portion such as from about 10% to 50% by weight of the stream is suspended in air or other oxygen-containing gas and introduced at a temperature of about 850° F. into the oxidizing regenerator. Preferably about one-third of the stream withdrawn from the coker is thus treated. Within the oxidizing regenerator, which may operate from a temperature of about 1000° F. to 2000° F. and preferably at about 1200° F. to 1500° F. the coke is burned to carbon monoxide and carbon dioxide and the iron sulfide is oxidized to form sulfur dioxide and the higher iron oxides. This reaction is conducted in the oxidizing regenerator in the presence of fluidized solids whereby a level is maintained within the vessel. From below this level and from that part occupied by the suspended solids is removed a continuous stream of solids consisting predominantly of the higher iron oxides at a temperature of about 1700° F. A portion of this is combined with the higher iron oxide, iron sulfide and coke removed from the coking vessel and recirculated to the oxidizing regenerator to effect temperature control. The remaining quantity is introduced directly into the coker where a carbonaceous deposit of coke is laid down on the particles to permit iron oxide reduction and a portion of which is converted to iron sulfide and treated as just above described.

The remaining portion of iron oxide, iron sulfide and coke removed from the coker comprises the major portion of the stream, from about 50% to about 90% by weight, is introduced into the reducing regenerator which may operate at a temperature of about 1400° F. and 1800° F. In transporting this fraction of solids removed from the coker to the reducing regenerator the solids may be suspended in a hydrocarbon gas or a producer gas and introduced as a fluidized system into the reducing regenerator. Within the reducing regenerator at a temperature of about 1750° F. iron oxide is actively reduced to elemental iron by the action of hydrocarbon gas which may contain considerable quantities of methane and ethane and may, if desired, comprise desulfurized gas produced as the lightest product from the coker bubble tower as previously described. The operation of the reducing regenerator is preferably such that the gas produced therein contains carbon monoxide and carbon dioxide in a molar ratio of about 3.0 or more and hydrogen and water vapor in a ratio of preferably 2.0 or more. A level of fluidized solids is maintained within the reducing regenerator from above which gases produced in the production reaction are withdrawn. From below this level is withdrawn a stream of solids comprising finely divided iron.

The gas removed from the upper portion of the reducing regenerator passes through a separator wherein it is freed from suspended solids and the solids-free gas comprises a producer gas containing substantial quantities of carbon monoxide and hydrogen. This gas may be employed as fuel, as a source of hydrogen, or with a moderate amount of purification as a source of a mixture of carbon monoxide and hydrogen which may be employed as a synthesis in a catalytic carbon monoxide hydrogenation conversion for the production of synthetic organic chemicals and liquid fuels. Such catalytic conversions are typified by the I. G.-Bergius process and the Fischer-Tropsch process.

A stream of finely divided iron containing some iron oxides is removed from the lower portion of the reducing regenerator and a part of

this stream is recirculated with the material introduced into the reducing regenerator in order to maintain temperature control. The remaining portion is cooled such as by passing through a waste heat boiler and is subjected to a magnetic separation or other separation wherein a stream of substantially pure elemental iron particles is recovered. The nonmagnetic material may be returned to the process for retreatment since an appreciable quantity of this may comprise oxides and sulfides of iron of relatively lower magnetic susceptibility. The finely divided iron is introduced at a controlled rate into a mixer to which is also added a controlled quantity of water and at least part of the coker distillate hydrocarbons obtained as products from the coker bubble tower. A slurry of this material is prepared in the mixer in which the ratio of iron to water is such that under conditions in the hydrogenation reactor iron will react with the water to produce a sufficient quantity of hydrogen to hydrogenate to the desired extent the unsaturated olefinic and aromatic hydrocarbon constituents present in the coker distillate. This material is removed from the mixer by means of a high pressure pump and passed through a heater capable of quickly increasing the temperature of the slurry to between about 500° F. and 1200° F. depending upon the nature of the coker distillate and the type and severity of hydrogenation desired. Temperatures of the order of 700° F. to 850° F. are suitable for moderate hydrogenation of olefinic constituents while temperatures in the upper portion of the range such as from 850° F. to 1100° F. are well adapted to effect cracking in the presence of hydrogen in which case a thermal decomposition of the hydrocarbons in the coker distillate is effected accompanied by immediate hydrogenation of the hydrocarbon fragments formed.

The hydrogenation operation is preferably carried out at superatmospheric pressures which, for example, may be as high as 1000 atmospheres or 15,000 pounds per square inch. Suitable operating pressures for the hydrogenation reaction may run lower than this maximum such as between about 250 pounds per square inch and 7000 pounds per square inch. Under these conditions of pressure and temperature the hydrogenation not only saturates the unsaturated hydrocarbon constituents present, but also decomposes sulfur, nitrogen and oxygen derivatives of hydrocarbons with the formation of hydrogen sulfide, ammonia, and water, respectively. The hydrogen sulfide, at least in part, is found in the hydrogenation reactor effluent as iron sulfide, while the ammonia formed accumulates in the unreacted water phase. The hydrogenation reactor is preferably provided with means for maintaining a continuous and efficient agitation of the contents of the vessel in order to insure uniform treatment and to prevent settling of the solids contained in the system.

The hydrogenation reactor effluent comprises a hydrogenated oil phase, unreacted water and solid particles comprising iron oxide, iron sulfide, and possibly some unreacted elemental iron. This entire material is introduced into a hydrogenated product bubble tower or other means of separation in which the hydrocarbon phase of the hydrogenator effluent is fractionated into portions having any desired boiling range. Depending upon the severity of the hydrogenation conditions, a variable quantity of gas containing saturated hydrocarbon gases may be produced. This gas is removed from the bubble tower as

an overhead product, cooled, and the normally gaseous constituents are separated from the condensate. This condensate comprises a hydrodesulfurized gasoline, a portion of which is returned to the bubble tower as reflux while the remainder is produced from the column as a gasoline product. Also removed from the column is an aqueous phase containing ammonium hydroxide. A gas oil product may be also produced which may have a boiling range from about 400° F. to 800° F. The higher boiling hydrocarbon constituents are produced as a hydrogenated residuum from the lower part of the bubble tower and carries with it iron oxide and iron sulfide formed from the elemental iron during the hydrogenation reaction. This residuum is preferably treated to recover the iron compounds and may be combined with the heavy oil as feed stock to the process and returned therewith to the coking vessel.

This modification of the process, according to this invention permits a substantially complete conversion of low value high density oils to desirable hydrocarbon fractions uncontaminated by sulfur, having lower boiling ranges and suitable for internal combustion engine fuels or as feed stock in the preparation of high quality lubricating oils and lubricating greases. The usual hydrogen compression facilities and the expensive sensitive catalyst required in some hydrogenation processes are hereby eliminated.

In the foregoing modifications of the process of this invention it has been found desirable, particularly in those cases when heavy or viscous hydrogenated residuums are formed which carry suspended solid particles, to convey a diluent oil into the hydrogenator bubble tower to assist in conveying this residuum. Recycling the coker bubble residuum as the hydrogenated residuum diluent has been found effective. Generally, the quantity of hydrogenated residuum is not large and not sufficient to carry the amount of solids present.

Another modification of the process of this invention exists in which a substantially complete vaporization of the hydrogenated effluent is effected to permit quick separation of the solid particles from the product.

A high density oil such as low A. P. I. gravity crude petroleum is combined with a coker bubble tower residue and with a hydrogenated residuum containing a small quantity of iron oxide particles and the mixture is heated to a temperature between about 700° F. and 1200° F. and introduced into the coking reactor. Higher iron oxide such as Fe_3O_4 and Fe_2O_3 produced from iron sulfide in the oxidizing regenerator is also introduced into the coking reactor in which the deposit of coke is laid down on the particles. Lower molecular weight unsaturated hydrocarbon fractions are simultaneously formed. The hydrocarbons thus produced are fractionated in a coker bubble tower with the production of gas, coker gasoline, and coker gas oil. The coker distillate is employed as feed stock to the hydrogenation unit and includes the gasoline, gas oil, and other fractions.

The coke-laden iron oxide passes from the coking vessel to the reducing regenerator into which air and part of the gas produced from the coker bubble tower are introduced. The reducing regenerator is a vessel in which a fluidized suspension of solids is maintained with the existence of a level of solids below which carbon oxidation and carbon reduction reactions are ef-

fect. A stream of iron particles substantially free of carbon and containing iron sulfide, ash and sodium chloride in minor amounts, is removed. The gas produced from the upper portion of the reducing regenerator contains a high concentration of carbon monoxide and also contains hydrogen and comprises a suitable producer gas which may be used as fuel or in the conversion of hydrogen sulfide or sulfur dioxide to elemental sulfur in a suitable reactor.

This stream of solid particles removed from the reducing regenerator is divided into two fractions, the major proportion of which is combined with the proper quantities of coker distillate and with water for introduction into the hydrogenation step of the process. The minor fraction is subjected to the action of the magnetic separator by means of which the ash and sodium chloride contents are separated from the iron compounds. The ash and salt-free matter obtained in the magnetic separator is combined with the major portion referred to previously and employed in the hydrogenation reaction.

A slurry is prepared containing coker distillate, water, and iron in the proper proportions so that the reaction of iron with water will produce a quantity of hydrogen sufficient to effect the desired degree of coker distillate hydrogenation. This slurry is picked up by a high pressure multistage pump and is passed together with additional water, if desired, at a controlled rate through a heater capable of raising the temperature of this mixture to between about 500° F. and about 1200° F. For the hydrogenation of a coker distillate prepared from a low A. P. I. gravity crude petroleum such as that obtained from the Santa Maria Valley of California, a hydrogenation temperature of about 700° F. to 800° F. is desirable and a pressure of about 5000 to 7000 pounds per square inch although pressures as high as about 1000 atmospheres or 15,000 pounds per square inch may be used.

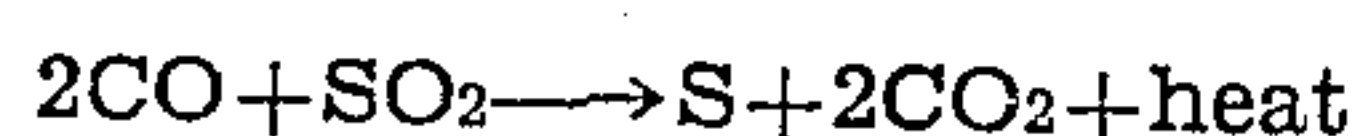
The heated mixture at superatmospheric pressure is passed from the heater into a hydrogenation reactor which preferably is provided with means for maintaining the liquid contents thoroughly agitated and the solid particles suspended in the fluid. It is highly desirable to maintain a completely liquid phase hydrogenation. Within the hydrogenation vessel under conditions of temperature and pressure given above, water readily reacts with metallic iron with the evolution of hydrogen and the formation of iron oxide. The hydrogen reacts with the coker distillate to be hydrogenated before molecular hydrogen (2-hydrogen atoms per molecule) is formed. The freshly formed hydrogen is known as atomic or nascent hydrogen. By consuming the hydrogen immediately and while it is in its atomic state, a highly efficient degree of coker distillate hydrogenation is effected. It is also possible in the hydrogenation reactor under temperatures above 800° F. to effect a destructive hydrogenation in which the boiling range of the hydrogenated product is lower than that of the coker distillate being hydrogenated and the hydrocarbon produced from the reactor may be readily vaporized.

A desulfurization reaction also occurs simultaneously with the hydrogenation whereby sulfur-containing hydrocarbon molecules are decomposed and the fragments hydrogenated with the formation of hydrogen sulfide and of hydrocarbons. At least a part of the hydrogen sulfide thus formed reacts with the iron or the iron oxide to form iron sulfide which is removed with

the hydrogenated hydrocarbons from the reactor. Oxygen and nitrogen derivatives of hydrocarbons are also decomposed with the formation of water and ammonia, respectively. The water thus formed may react with additional quantities of iron to form hydrogen while the ammonia dissolves in any excess water and may be recovered as an aqueous phase from the hydrogenated material.

The hydrogenated hydrocarbon stream passing from the hydrogenation reactor is suddenly depressured from the superatmospheric operating pressure through one or a plurality of expansion valves to a pressure at or near atmospheric pressure such as from about 15 to 100 pounds per square inch absolute. The material is subsequently passed through a coil in a heater and the combination of the expansion and the heating effects a substantially complete vaporization of the hydrogenated effluent. The gaseous hydrocarbon stream thus produced carries with it suspended particles of iron which may be unreacted and with the iron oxide and iron sulfide. This vapor stream passes into a suitable separator which may comprise a cylindrical tower with a centrifugal separator supported in the upper portion thereof. By means of the separator the suspended solid matter is removed and passes over a series of baffles down through the tower countercurrent to a stripping gas such as steam which serves to remove remaining traces of liquids or gases from the solids.

The solids are removed from the lower part of the vessel, suspended in a stream of air and conveyed as a suspension into the oxidizing regenerator referred to above in which the oxidation of iron sulfide is effected in a fluidized system. The combustion of iron sulfide to form iron oxide results in gases containing considerable quantities of sulfur dioxide. This gas may be chemically reduced by reaction with carbon monoxide by combining oxidizing regenerator effluent with the proper proportion of reducing regenerator effluent or producer gas so that the following reaction occurs:



A substantial liberation of heat results which may be employed in a waste heater boiler to generate high pressure steam and simultaneously cooling the sulfur-bearing gases to below about 250° F. to permit centrifugal or electrical precipitation of the solid sulfur particles.

Returning now to the hydrogenated effluent separator, a vapor stream comprising vapor phase hydrocarbon and water is removed from the separator and introduced into the hydrogenator bubble tower whereby a fractionation of the hydrogenated effluent is effected. Gases are produced from the upper portion of the tower as well as a hydrogenated and desulfurized gasoline, gas oil and other hydrocarbon fractions of different boiling range. From one tray in the tower an aqueous phase containing ammonium hydroxide may be produced. The hydrogenated hydrocarbon fractions thus produced comprise suitable raw materials for the preparation of high grade internal combustion engine fuels, solvents, lubricating oil and lubricating greases, etc. A small amount of residual material remains in the system and may be produced as a bottoms product from the hydrogenator bubble tower and is returned and combined with the feed stock to the system whereby it is recoked.

The fundamental advantage of this modification lies in the hydrogenation step wherein a substantially complete separation of the unreacted iron if any and the solid iron compounds from the hydrogenated product is effected by expanding the hydrogenator effluent from its superatmospheric pressure to substantially completely vaporize the stream followed by a centrifugal separation of the solid products suspended in the gas. This modification of the operation is readily carried out particularly when the lower boiling products are desirable such as the gasolines and gas oils.

In the modifications of the process of this invention as given above the operating pressures in all cases except that of the hydrogenation are at or near atmospheric pressure. It is preferable to operate a fluidized system at pressures somewhat in excess of that of the atmosphere to aid in effecting proper control of the operation. Consequently the preferred pressure range for the operation of the fluidized coker, the reducing regenerator and the oxidizing regenerator is from about zero pounds to about 100 pounds per square inch gauge, a pressure of about 30 pounds per square inch gauge being well suited to this particular operation. The operation of the coker bubble tower and the hydrogenated effluent bubble tower in which hydrogenation distillations are effected are preferably operated at pressures in the same approximate pressure range.

As previously stated, the hydrogenation operation may be carried out at superatmospheric pressures as high as about 1000 atmospheres or about 15,000 pounds per square inch. Operating pressures for the hydrogenation step in the range of from about 3000 to 10,000 pounds per square inch are well suited to effecting the desired results and operating pressures of from about 4000 to about 7500 pounds per square inch have been found suitable.

In each modification, hydrogen generation arises from the reaction of water with a metal above hydrogen in the electromotive series, that is with a metal capable of displacing hydrogen from water forming a metal oxide reducible by carbon. In the modifications described above iron has been set forth as this metal. There are, however, other metals which are capable of effecting this reaction to the desired extent. Among these metals are zinc, cobalt, nickel, manganese, and the like. This includes the metals of atomic Nos. 25 through 30 of Mendeleeff's Periodic Table of the elements with the exception of copper.

In the modification of the process of this invention described above, a substantially complete desulfurization of a hydrocarbon fraction may be effected by hydrogenation. This is accomplished in the hydrogenation reactor under the temperature and pressure and other conditions described above. Another modification exists by means of which desulfurization may be at least partially effected in the coking reactor in which at least a part of the elemental iron produced from the reducing regenerator is combined with the hydrocarbon feed stream passing into the coker. The presence of elemental iron at coking temperatures sufficient to thermally decompose sulfur-containing hydrocarbon compounds permits the hydrogen sulfide thus liberated to readily convert part of the iron to iron sulfide. The immediate effect of incorporating elemental iron with the hydrocarbon stream to the coker is that of reducing the sulfur content of the hydrocarbon

fractions produced from the coker bubble tower, and reducing the hydrogen consumption in the hydrogenation step of the combination process.

In the modifications of the process of this invention described above, exclusive reference has been made to the treating of heavy gravity crude petroleum by means of which these hydrocarbons are coked in the presence of iron oxide, the coke-laden iron oxide is suitably treated to reduce the iron oxide to iron, and the iron is reacted with water in the presence of at least part of the hydrocarbon products obtained during the coking reaction to form hydrogenated and desulfurized liquid and hydrocarbon fractions. It should not be understood that the process of this invention is exclusively applicable to the treating of petroleum hydrocarbons since similar desirable results may be brought about in employing the heavy gravity oils and tars obtained from coal distillation as feed stock. These tars and oils are essentially aromatic in nature containing high molecular weight condensed ring structures and include such materials as benzene, toluene, xylene, naphthalene, anthracene, phenanthrene, chrysene, picene, and other polynuclear aromatic as well as heterocyclic compounds. Various condensed structures such as indene and fluorene, as well as the higher molecular weight aromatic acids known as phenols and the higher molecular weight aromatic bases of the pyridine type also occur. By employing such coal tar fractions as feed stock in the process of this invention, desirably lower boiling hydrocarbon fractions may be obtained which may contain a variable quantity of residual aromatic hydrocarbons and may also contain variable quantities of cyclic saturated hydrocarbons of the naphthene type as well as paraffinic hydrocarbons depending upon the severity of the coking and of the hydrogenation step. Highly desirable hydrocarbon fractions may be readily obtained from this type of feed stock.

The process, according to this invention may be further applied to the hydrogenation of normally solid carbonaceous materials of which examples are bituminous coal, lignite, peat, brown coal, and the like. The process of this invention is modified to the extent that the carbonaceous material or coal to be treated is finely pulverized in a suitable grinding mill and mixed with a tar recycle to form a paste or a liquid suspension of coal solids in the oil. This tar recycle may be one obtained from the coker wherein the paste is coked with the liberation of further quantities of aromatic type coal tars or it may be a residual oil from the hydrogenation effluent bubble tower which desirably is reprocessed. During the operation of this modification of the process iron oxide produced from the oxidizing regenerator is combined with the paste and introduced into the coker or it may be introduced into the coker directly. The hydrocarbon oils liberated from the coal during coking are subsequently mixed with iron, for example, and water and hydrogenated under high pressure as previously described. Such materials as oil sand, tar sand, oil-soaked diatomite may be treated in a manner similar to that described above for handling carbonaceous solids such as coal.

The process of the present invention described in detail above permits the ready conversion of carbonaceous materials whether they are solids or liquids to desirable hydrocarbon fractions substantially free of contaminating elements by a

combined operation of coking in the presence of a metal oxide, depositing a carbonaceous solid on the metal oxide, and hydrogenating the thermal pyrolysis product obtained during the coking operation by reacting the metal with water under high pressure and temperature to produce hydrogen. The process eliminates the disadvantages inherent in previous hydrogenation processes, namely, the requirements for expensive and sensitive hydrogenation catalysts the requirement for extensive hydrogen compression facilities, and others.

A particular embodiment of the present invention has been described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be made by those skilled in this particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

We claim:

1. A process which comprises pyrolyzing a hydrocarbon oil in the presence of spent solid particles to form a hydrocarbon pyrolysis product and coke-laden particles, said spent particles being formed by reacting regenerated particles with water to liberate hydrogen therefrom, reacting said coke with said spent particles to form regenerated particles in the presence of oxygen-containing gas, combining at least a portion of said regenerated particles with at least a portion of said pyrolysis product, subjecting the mixture thus formed to hydrogenating conditions of pressure and temperature in the presence of water in the liquid phase thereby hydrogenating said pyrolysis product and forming said spent solid particles, separating hydrogenated oils from said spent particles and recirculating said particles.

2. A process which comprises coking a hydrocarbon oil in the presence of fluidized particles of an oxide of a metal above hydrogen in the electromotive series to form coke-laden metal oxide particles and a coker distillate, said metal oxide being in a higher oxidation state, separating coke-laden particles from said coker distillate, heating said coke-laden iron oxide particles to remove coke and regenerate the metal oxide particles to a lower oxidation state, reacting the regenerated lower metal oxide particles with water in the presence of at least a portion of said coker distillate thereby hydrogenating said distillate and forming said metal oxide of higher oxidation state, separating this higher metal oxide from the hydrogenated product and recirculating said higher metal oxide.

3. A process according to claim 2 wherein said hydrocarbon contains suspended carbonaceous solids.

4. A process according to claim 2 wherein said hydrogenated product is fractionated leaving a hydrogenated residuum, suspending finely divided solid carbonaceous solids therein and recirculating the mixture thus formed to hydrogenate said solid carbonaceous solids.

5. A process according to claim 4 wherein said finely divided carbonaceous solids are particles of coal.

6. A process which comprises coking a hydrocarbon oil in the presence of fluidized particles of a higher oxide of iron to form coke-laden higher iron oxide particles and a coker distillate, separating said particles from said distillate, fluidizing said coke-laden higher iron oxide particles at a temperature sufficient to cause reaction between

the higher oxide and the coke thereby forming coke-free reduced particles containing iron in a lower oxidation state capable of reacting with water to liberate hydrogen, contacting at least a portion of said coker distillate with said coke-free reduced particles thus formed in the presence of water in the liquid phase thereby hydrogenating said coker distillate to form said higher iron oxide and a hydrogenated product, distilling said hydrogenated product to recover hydrogenated hydrocarbon fractions therefrom leaving a hydrogenated residuum containing particles of said higher iron oxide and combining said hydrogenated residuum with said hydrocarbon oil to be coked.

7. A process according to claim 6 wherein said higher iron oxide particles are reduced with coke to ferrous oxide (FeO).

8. A process according to claim 6 wherein said higher iron oxide particles are reduced with coke to iron.

9. A process which comprises coking a hydrocarbon oil contaminated with sulfur compounds in the presence of fluidized particles of ferric oxide to form a coker distillate contaminated with sulfur compounds and coke-laden ferric oxide particles, separating said particles from said distillate, fluidizing coke-laden particles of ferric oxide at an elevated temperature to effect reduction of the ferric oxide to elemental iron, separating iron particles thus formed, contacting at least a portion of said coker distillate with said elemental iron particles in the presence of water in the liquid phase whereby said coker distillate is hydrogenated and desulfurized by hydrogen formed through the interaction of water and said iron forming a desulfurized hydrogenated product, iron sulfide, and ferric oxide, distilling said hydrogenated product to recover desulfurized hydrocarbon fractions, separating particles of iron sulfide formed in desulfurizing said coker distillate, fluidizing said particles of iron sulfide in an oxygen-containing gas thereby forming ferric oxide and sulfur dioxide and recirculating the ferric oxide thus formed.

10. A process which comprises coking a hydrocarbon oil contaminated with hydrocarbon compounds of sulfur in the presence of fluidized particles of ferric oxide to form a sulfur compound contaminated coker distillate and ferric oxide particles laden with coke, separating said particles from said distillate, fluidizing said coke-laden ferric oxide particles in contact with an oxygen-containing gas at an elevated temperature to form carbon monoxide and particles of elemental iron, separating iron particles thus formed, reacting said particles of iron with water in the presence of at least a portion of said coker distillate in the liquid phase thereby hydrogenating and desulfurizing said coker distillate forming iron sulfide and ferric oxide, distilling the hydrogenation product to recover a desulfurized hydrocarbon fraction therefrom, recovering particles of iron sulfide, fluidizing said iron sulfide in an oxygen-containing gas thereby oxidizing said iron sulfide forming sulfur dioxide and ferric oxide, separating said ferric oxide particles, recycling said ferric oxide, combining at least a portion of the carbon monoxide produced in reducing said ferric oxide with at least a portion of the sulfur dioxide bearing gases produced by iron sulfide oxidation, and effecting an elevated temperature reaction of said carbon monoxide with said sulfur dioxide to produce elemental sulfur.

11. A process according to claim 10 wherein the effluent gases from the reaction involving carbon monoxide and sulfur dioxide are cooled to a temperature above about 225° F. to separate sulfur in liquid form.

12. A process according to claim 10 wherein the effluent gases from the reaction involving carbon monoxide and sulfur dioxide are cooled to a temperature below about 250° F. to separate finely divided particles of sulfur in solid form.

13. A process according to claim 10 which comprises contacting the residual gases from the carbon monoxide reaction with sulfur dioxide which contain unreacted quantities of sulfur dioxide and hydrogen sulfide with the reduced particles produced by elevated temperature reaction of said coke-laden ferric oxide to form further quantities of iron sulfide and the like, and recirculating said iron sulfide to the process to effect a substantially complete recovery of the hydrocarbon compound of sulfur as elemental sulfur.

14. A process according to claim 10 including the step of combining ferric oxide produced in the oxidation of iron sulfide with said hydrocarbon oil to be coked to form further quantities of iron sulfide.

15. A process according to claim 10 including the step of magnetically separating particles of iron sulfide from said hydrogenation product.

16. A process which comprises coking a hydrocarbon oil in the presence of fluidized particles of Fe_3O_4 to form a coker distillate and coke-laden Fe_3O_4 particles, fluidizing said coke-laden Fe_3O_4 particles in heated gases thereby forming carbon monoxide and reduced iron oxide particles in a lower state of oxidation, separating said reduced particles from said carbon monoxide gases, reacting said reduced particles with water in the liquid phase under superatmospheric pressure in the presence of at least a portion of said coker distillate to hydrogenate olefinic constituents thereof while reforming said Fe_3O_4 and desulfurizing said distillate forming iron sulfide, fractionating the hydrogenated product to obtain a hydrogenated residuum containing Fe_3O_4 and iron sulfide, combining said hydrogenated residuum with said hydrocarbon oil to be coked, magnetically separating iron sulfide from circulating solids streams in the process, fluidizing said iron sulfide in an oxygen-containing gas thereby forming sulfur dioxide and particles of Fe_2O_3 at an elevated temperature, contacting said particles of Fe_2O_3 with at least a portion of said carbon monoxide gases produced in the Fe_3O_4 reduction thereby reducing said particles of Fe_2O_3 to Fe_3O_4 and recirculating the particles of Fe_3O_4 thus formed.

17. A process which comprises establishing a fluidized coking zone, a fluidized reducing regenerating zone, a fluidized oxidizing regenerating zone and a liquid-phase hydrogenating and desulfurizing zone, combining a hydrocarbon oil contaminated with sulfur compounds with a coker distillate residuum and a hydrogenated residuum containing suspended particles of solid iron compounds such as iron oxides and iron sulfide, heating the combined hydrocarbon oil and residuum stream, contacting the heated stream with heated particles of Fe_3O_4 prior to introducing the mixture thus formed into said fluidized coking zone to form coke-laden Fe_3O_4 particles and a coker distillate, separating coke-laden particles of Fe_3O_4 from said coker distillate, distilling said coker distillate to produce said coker

distillate residuum and selected hydrocarbon fractions of said coker distillate, introducing the separated particles of Fe_3O_4 into said fluidized reducing regenerating zone wherein said Fe_3O_4 is reduced to an iron compound in a lower oxidation state forming a gas containing carbon monoxide, magnetically separating the reduced iron compound from relatively less magnetic solids such as iron sulfide removed from the reducing regenerator, combining the reduced iron compound thus recovered with at least a portion of said coker distillate, reacting said iron compound with water in said hydrogenating zone at an elevated temperature in the liquid phase thereby hydrogenating said coker distillate and simultaneously effecting a coker distillate desulfurization forming iron sulfide, distilling the hydrogenated product thus formed to separate desirable sulfur-free hydrocarbon fractions thereof leaving a hydrogenated residuum containing Fe_3O_4 and iron sulfide, recirculating said hydrogenated residuum to said fluidized coking zone, oxidizing said iron sulfide magnetically separated from said reducing regenerating zone in said fluidized oxidizing regeneration zone to form ferric oxide and a gas containing sulfur dioxide and recirculating the Fe_3O_4 thus formed to said fluidized reducing regeneration zone.

18. A process according to claim 17 wherein at least a portion of the solids withdrawn from said fluidized reducing regeneration zone are introduced with the combined hydrocarbon streams to said fluidized coking zone wherein at least a portion of the sulfur compounds are decomposed to form iron sulfide.

19. A process according to claim 17 wherein hydrocarbon compounds of nitrogen are present in said hydrocarbon oil and are hydrogenated in said liquid phase hydrogenation zone in the presence of water to form ammonia, said ammonia being recovered as ammonium hydroxide upon distillation of the hydrogenated product from said hydrogenated zone.

20. A process according to claim 17 wherein said coker distillate is introduced into a distillation zone to produce an overhead gas stream containing normally gaseous hydrocarbons, contacting said gas thus produced with an absorber oil to remove normally liquid hydrocarbon compounds leaving a dry gas, desulfurizing said dry gas to remove hydrogen sulfide, and introducing the desulfurized dry gas thus formed directly into said fluidized reducing regeneration zone.

21. A process according to claim 17 including the steps of dividing the reduced particles removed from said reducing regenerating zone into a major portion and a minor portion, introducing said major portion with said coker distillate directly into said hydrogenating and desulfurizing zones, subjecting the minor portion to magnetic separation of iron sulfide therefrom, introducing the thus separated iron sulfide into said oxidizing regenerating zone, and passing the remaining part of said minor portion to said hydrogenating and desulfurizing zone.

22. A process according to claim 17 wherein catalytic quantities of a hydrogenation catalyst are circulated with the stream of iron compound particles.

23. A process which comprises establishing a fluidized coking zone, a fluidized reducing regeneration zone, a fluidized oxidizing regeneration zone and a liquid phase hydrogenation zone, combining a hydrocarbon oil containing hydrocarbon compounds of sulfur and nitrogen with a

coker distillate residuum and a hydrogenated product residuum containing suspended solid particles of Fe_3O_4 and FeS , heating the combined liquid stream thus formed, contacting the heated stream with heated particles of Fe_3O_4 in said fluidized coking zone to form a coker distillate and coke-laden Fe_3O_4 and FeS particles at a temperature between about 700°F . and 1200°F . and at a pressure of between zero and 250 pounds per square inch gauge, distilling said coker distillate to recover said coker distillate residuum which is recirculated to the coking zone, separating coke-laden particles of Fe_3O_4 and FeS from said fluidized coking zone, introducing said coke-laden particles into said fluidized reducing regeneration zone wherein a Fe_3O_4 reduction is effected at a temperature of from about 1400°F . to about 1800°F . to form coke-free particles containing iron in lower oxidation states and a gas containing carbon monoxide, removing the reduced particles thus formed from said reducing regeneration zone, separating FeS from said particles containing iron in a lower oxidation state, fluidizing said FeS in an oxygen-containing gas in said oxidizing regeneration zone at a temperature between 1000°F . and about 2000°F . to form a gas containing sulfur dioxide and particles of Fe_3O_4 , recirculating said Fe_3O_4 to said reducing regeneration zone, combining a portion of carbon monoxide gases from said reducing regeneration zone with a portion of sulfur dioxide gases from said oxidizing regeneration zone in a controlled ratio to form elemental sulfur combining at least a portion of said coker distillate with said reduced particles containing iron in lower oxidation states, reacting said particles with water at a temperature of from 500°F . to about 1200°F . at a pressure up to about 15,000 pounds per square inch to hydrogenate and desulfurize said coker distillate thereby forming FeS from said hydrocarbon compounds of sulfur and ammonia from said hydrocarbon compounds of nitrogen, distilling the hydrogenated product to recover desulfurized hydrogenated hydrocarbon fractions thereof leaving a hydrogenated residuum containing FeS and Fe_3O_4 , and recirculating said hydrogenated residuum with said hydrocarbon oil and said coker distillate residuum to said fluidized coking zone.

24. A process according to claim 23 wherein said reduced particles containing iron in a lower oxidation state removed from said reducing regeneration zone comprise particles of ferrous oxide (FeO) formed in said reducing regeneration zone while maintaining a circulating gas stream in said reducing regeneration zone having a carbon monoxide to carbon dioxide ratio of between 0.5 to 3.0 and while introducing a stream of hydrocarbon gas into said reducing regeneration zone.

25. A process according to claim 23 wherein said reduced particles removed from said reducing regeneration zone comprise elemental iron produced in said reducing regeneration zone while maintaining therethrough a recirculating gas stream containing a carbon monoxide to carbon dioxide ratio of from about 2.5 to 5.0 and while introducing a stream of hydrocarbon gas into said reducing regeneration zone.

26. A process according to claim 23 wherein the particles of iron compound removed from said fluidized oxidizing regeneration zone comprise Fe_2O_3 and which is reduced to Fe_3O_4 by countercurrent contact with a part of the carbon

monoxide bearing gases at a temperature between 1400° F. and 1800° F. removed from said fluidized reducing regeneration zone and said Fe_3O_4 is subsequently recirculated.

27. A process according to claim 23 wherein said liquid phase hydrogenation zone is provided with a continuously recirculating stream of hydrogenated effluent containing suspended particles which is combined with said coker distillate containing particles of iron compound in its lower state of oxidation and is recirculated in sufficient quantities through a heating zone and subsequently through said liquid phase hydrogenation zone in the presence of water to effect a substantially instantaneous heating of said coker distillate and iron to temperatures between about 500° F. and 1200° F. required to effect hydrogenation and desulfurization.

28. A process according to claim 23 wherein said fluid to be hydrogenated comprises from about 5% to about 35% by weight of a water-oxidizable compound of iron such as iron and ferrous oxide (FeO), from about 2% to about 25% by weight of water and from about 30% to about 90% by weight of coker distillate, to which fluid has been added a small quantity of a hydrogenation accelerator selected from the group consisting of water-soluble halides of calcium, magnesium, iron, manganese and ammonium.

29. A process according to claim 23 which comprises combining said coker distillate with particles of an iron compound capable of reacting with water to liberate hydrogen to form a slurry, passing said slurry through a heating zone into said hydrogenation zone, separately heating water under superatmospheric pressure, introducing the heated water into said hydrogenation zone so that the hydrogenation reaction takes place completely within the hydrogenation zone.

30. A process according to claim 23 wherein the residual gases remain after the separation of elemental sulfur produced in the sulfur dioxide-carbon monoxide reaction contains unreacted sulfur dioxide which is recovered by the step of contacting such residual gases with the coke-free particles removed from the reducing regeneration zone.

31. A process according to claim 23 wherein said hydrogenated product is flash vaporized by reducing the pressure thereby separating the hydrogenated product into a vapor and a hydrogenated residuum containing iron sulfide and a higher iron oxide, distilling the vapor thus formed, and recirculating the hydrogenated residuum.

32. A process according to claim 31 wherein said hydrogenated product is substantially completely vaporized forming a vapor containing suspended solid particles, the steps of separating said solid particles from said vapor and recirculating the thus separated solids to said oxidizing regenerating zone.

33. A process which comprises thermally

pyrolyzing a hydrocarbon oil in the presence of particles of a higher oxide of iron and iron sulfide to form a coker distillate and coke-laden particles in a fluidized coking zone, separating said coke-laden particles from said coking zone, introducing between 50% and 90% by weight of the solids stream thus removed to a fluidized reducing regeneration zone in which the higher oxides of iron are reduced while maintaining a continuous gas recycle stream containing carbon monoxide through said reducing regeneration zone to form reduced particles, introducing between about 10% and about 50% of the solids stream to a fluidized oxidizing regenerator wherein said iron sulfide is oxidized to form further quantities of higher iron oxide, recirculating the higher iron oxide thus formed to said fluidized coking zone, combining said reduced particles separated from said fluidized reducing regenerator with at least a portion of said coker distillate, reacting said reduced iron compound particles in the presence of water at a temperature of about 750° F. and at a pressure as high as 15,000 pounds per square inch in the liquid phase to desulfurize and hydrogenate said coker distillate to form a hydrogenated product, and said higher iron oxide and iron sulfide, distilling said hydrogenated product to form desulfurized fractions thereof leaving a hydrogenated residuum containing said higher iron oxide and iron sulfide, and recirculating the residuum thus formed to said fluidized coking zone.

HOMER C. REED.
CLYDE H. O. BERG.
CHARLES B. LEFFERT.

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