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TREATMENT OF HYDROCARBONS WITH IODINE AND/OR HYDROGEN IODIDE FOLLOWED BY HYDROGENATION

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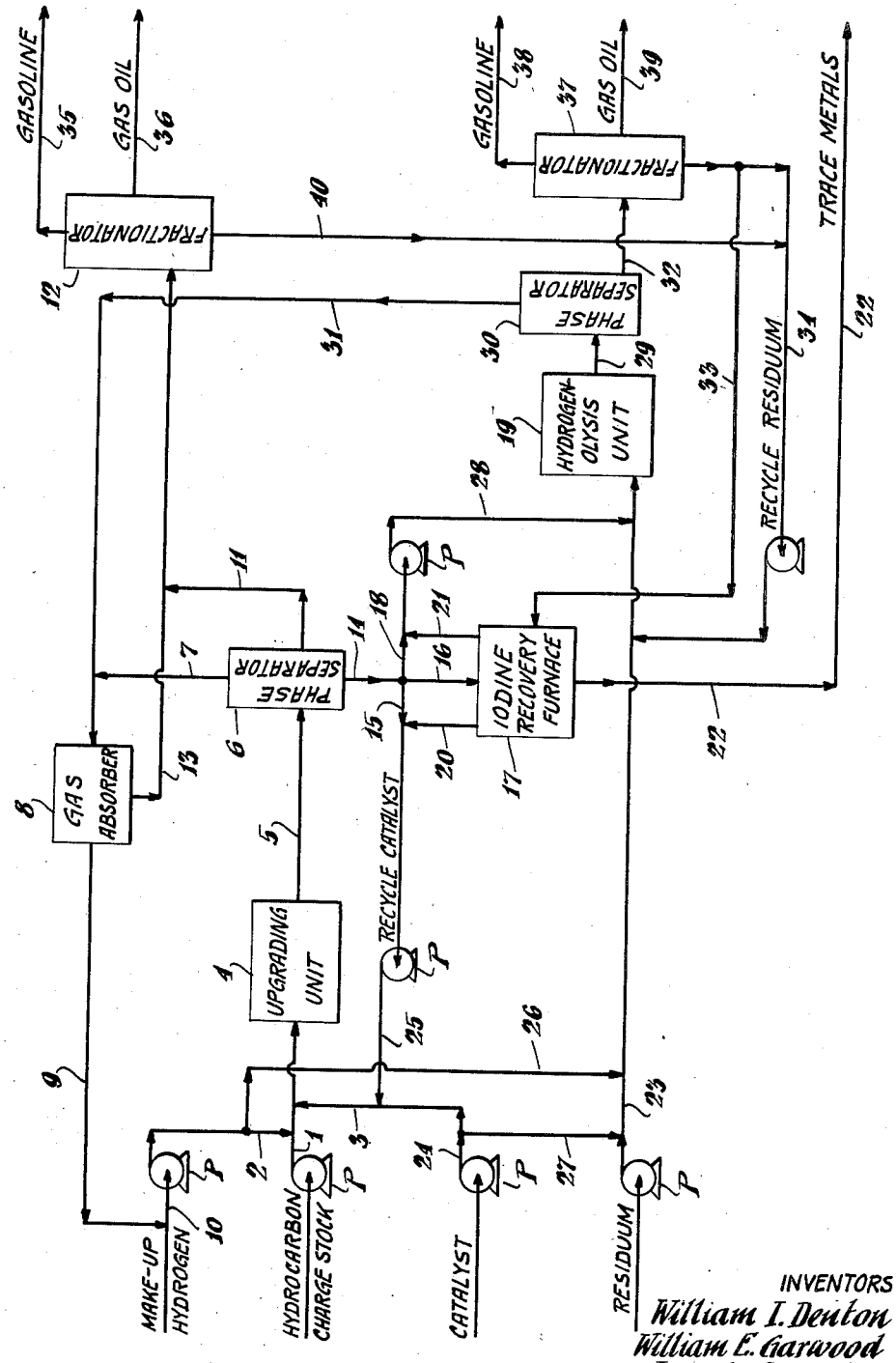

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TREATMENT OF HYDROCARBONS WITH IODINE AND/OR HYDROGEN IODIDE FOLLOWED BY HYDROGENATION

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This invention relates to treatment of low grade sulfur-containing hydrocarbon oils. More particularly, the present invention is directed to a process for converting and upgrading hydrocarbon oils of high sulfur, nitrogen, or metal content. The process described herein is especially applicable for treatment of residues and tars produced in various petroleum refining operations. These materials, which are normally disposed of as No. 6 fuel oil, traditionally yield a very poor return in comparison with that obtained from gasoline and light gas oils.

The presence of sulfur, nitrogen, and heavy metals in petroleum crudes and fractions thereof has heretofore been recognized as undesirable. Sulfur occurs in petroleum stocks generally in two principal forms, as mercaptans and as part of ring type compounds such as thiophene. The particular kind and amount of sulfur compound present in a petroleum hydrocarbon varies with the source and previous processing, if any, to which said petroleum hydrocarbon has been subjected. While non-refractory sulfur compounds, such as mercaptans, can be effectively removed by various treating operations, the removal of refractory sulfur compounds of the ring type has been much more difficult. These compounds, as is well known, are highly objectionable in hydrocarbon oils because of their bad odor and corrosive tendencies.

The presence of nitrogen compounds in hydrocarbon oils is also objectionable since they tend to destroy the activity of hydrocarbon conversion catalysts with which the oil may be brought into contact during various processing operations. Thus, in catalytic cracking of a hydrocarbon oil containing an appreciable amount of nitrogen compounds, the catalyst prematurely loses activity due to the poisoning effects of the nitrogen compounds.

Likewise, the presence of metals and metal compounds, such as those of copper, vanadium, nickel, and iron, in crude petroleum and various fractions thereof is highly undesirable since they impart corrosive properties to the oil, contribute to ash deposition in fuel oils and are responsible for catalyst deterioration when oils containing the same are used as charging stocks in catalytic cracking operations.

One method for upgrading and removing sulfur and other contaminants from hydrocarbon stocks has been by hydrogenation in the presence of a sulfur-resistant catalyst at elevated temperature and pressure whereby organic sulfur compounds present in the hydrocarbon charge are hydrogenated to hydrogen sulfide which is thereafter removed from the treated hydrocarbons. Such procedures have generally involved a considerable consumption of hydrogen, and the cost of supplying the hydrogen is an important factor influencing the economics of the process. In addition, in order to secure the required partial pressure of hydrogen, it has generally been essential to operate at elevated pressure, i. e., 3000 p. s. i. g. and higher, necessitating the use of relatively expensive steels in plant construction which, in turn imposes a further economic burden on the process. Moreover, while the above process has been employed with some success in treating low and medium boiling petroleum fractions, the process is totally unsatisfactory for sulfur removal from high boiling stocks, such as reduced crudes, cycle stock, cracking tars, shale oil, tar sands, and residua. These latter stocks are characterized by the formation of an appreciable quantity of carbonaceous material on the catalyst after a short on-stream period rendering the catalyst inactive. Since regeneration is expensive and since the period of activity is short, this process has not been commercially attractive.

It is accordingly an object of the present invention to provide an improved method for upgrading low grade crude oils contaminated with appreciable quantities of sulfur, nitrogen, and/or metals. A further object is the provision of an inexpensive method for upgrading heavy stocks such as residua. A still further object is to provide a commercially attractive combined process involving upgrading of low grade crude petroleum oils and treatment of heavy residua.

The above and other objects which will be apparent to those skilled in the art are achieved in accordance with the present invention. Broadly, the process described herein comprises treating hydrocarbon oils containing sulfur, nitrogen or metals with iodine, hydriodic acid or mixtures thereof at a moderately elevated temperature below that at which appreciable cracking of the hydrocarbon charge stock to lighter material is encountered, separating the resulting upgraded products from an iodine-rich tar containing the contaminants, by fractionation, to yield desulfurized gasoline, a gas oil low in sulfur and nitrogen and free of metals, and a residuum containing small amounts of iodine. Such residuum may be treated directly with hydrogen without further addition of catalyst if the iodine content thereof exceeds 0.1 percent by weight. The above residuum is generally treated with hydrogen in the presence of a catalyst which is the aforementioned tar or iodine regenerated from said tar. As a charge to the second stage of treatment involving hydrogenolysis, the residuum obtained from the first stage may be supplemented by additional petroleum residua from other sources. Such residua refers to the bottoms product after petroleum stock has been topped and the gas oil removed, i. e., that fraction boiling above 750° F. at atmospheric pressure. These residua are ordinarily of little value per se because of their high content of sulfur and ash and their high tendency to coke on heating. The process of the instant invention thus provides a combined process involving the upgrading of low grade crudes or other stocks which respond poorly to conventional refinery operations and the hydrogenolysis of refinery residuum, including cracking tars and other high boiling heavy stocks.

It has been discovered, in accordance with the present invention, that iodine, hydriodic acid, and mixtures thereof under particularly defined reaction conditions hereinafter set forth provide a highly efficient and selective means for effecting removal of sulfur, nitrogen, and heavy metal contaminants from hyrocarbon oils containing the same. It is contemplated that sulfur-containing hydrocarbon oils generally may be treated in accordance with the instant process. Thus, petroleum crudes, gas oils, and reduced crudes containing sulfur are effectively refined with resulting resulfurization and reduction in nitrogen and metal content. The process is particularly applicable in treating low grade stocks which contain heavy metals, nitrogen, and refractory type sulfur compounds not easily removed by conventional desulfurization processes, such as stocks derived from Trinidad, California, and Mexican crudes. In addition to the removal of sulfur and nitrogen, heavy metals, such as nickel, vanadium, and iron are removed from the hydrocarbon stocks undergoing the the treatment described herein.

Thus, the first step of the process involves contacting a petroleum crude or similar stock high in sulfur, nitrogen, and metal content with iodine, hydriodic acid, or a mixture of iodine and hydriodic acid. The treating reagent may be brought into contact with the charge in any suitable manner. Advantageously, iodine is added as a solid while hydriodic acid is used as an aqueous solution although it may be used as a solution in a low molecular weight alcohol or other solvent. It is particularly desirable to employ aqueous constant boiling hydriodic acid containing about 55 percent HI. The temperature in the first stage of treatment should be maintained within the approximate range of 500° F. to 850° F. Below about 500° F., substantially no refining action takes place, while at temperatures in excess of 850° F., appreciable cracking or degradation of the hydrocarbon stock takes place, resulting in a lower liquid recovery and higher gas-make with little additional refining. In particular, it is desirable to employ a temperature between about 700° F. and about 800° F. The pressure may vary widely, depending upon the particular oil stock undergoing treatment and the temperature used but, in general, will be within the range of about 100 to about 3000 p. s. i. g. The time of reaction is dependent largely on the particular temperature employed and may range from 0.01 to 10 hours, longer reaction times being employed with the use of lower temperatures. It is particularly feasible to operate in a continuous manner and in such instances a space velocity of about 0.2 to about 4 is employed.

The amount of iodine, hydriodic acid or mixtures thereof required for refining of the oil charge depends largely on the extent of contamination. It is usually advantageous to use an excess of reagent and to recover the unused portion thereof, followed by recyling. The amount of reagent, i. e., iodine or hydriodic acid, employed is generally between about 0.1 and about 30 percent by weight, and preferably between about 1 and about 15 percent by weight, of the oil undergoing treatment. Solutions of iodine in hydriodic acid may also be used with advantage in the present process. Under such conditions of operation, the concentration of iodine in 55 percent aqueous hydriodic acid solution is preferably between about 40 and about 60 percent by weight. With the use of iodine, the presence of hydrogen in the reaction mixture was found to increase liquid recovery and to increase the extent of refining. Under such conditions of operation, it is desirable to employ hydrogen, preferably between about 100 and about 3000 p. s. i. g. pressure.

The products resulting from the above treatment comprise gases, the treated liquid hydrocarbon product, and a tarry precipitate. The latter tar, containing the major portion of sulfur, nitrogen, and metals of the charge stock, also contains the iodine. This tar may alternatively be recycled as the catalyst in the above step, employed as the catalyst in the hydrogenolysis step described below, or burned to recover iodine and the trace metals contained therein. The treated liquid hydrocarbon product is fractionated to yield desulfurized gasoline, a gas oil low in sulfur and nitrogen and free of metals and a residuum containing small quantities of iodine which is treated in the second stage of the operation. The gaseous reaction product contains a substantial proportion of light hydrocarbons which may be collected for use as a fuel gas.

The second stage involves hydrogenolysis of the residuum obtained in the first stage either alone or in admixture with additional straight run residua from another source. As a catalyst for the second stage, the iodine-rich tar from the first stage or regenerated iodine from such tar is employed. The amount of iodine-rich tar employed is generally between about 0.5 and about 25 percent by weight of the residuum charge. In those instances where regenerated iodine is employed, the amount thereof is ordinarily between about 0.1 and about 5.0 percent by weight of the residuum charge. A minor

amount of coke, which is burned to recover iodine, is formed in the second stage, in addition to gasoline, gas oil, and unconverted residuum. The reaction conditions during hydrogenolysis involve a temperature in the approximate range of 750° F. to 1000° F., and preferably between about 800 and about 950° F., a pressure in the approximate range of 200 to 3000 p. s. i. g., and preferably between about 500 and about 1500 p. s. i. g., and a space velocity of between about 1 and about 10.

The operation may be carried out batch-wise by thoroughly mixing the oil charge with the hydriodic acid or iodine reagent under the above-specified conditions in the first stage and fractionating the resulting upgraded product to useful products and a residuum, and recovering the resulting iodine-rich tar. The residuum so obtained may thereafter be subjected to hydrogenolysis in the presence of the aforementioned tar as a catalyst.

The operation may also be carried out continuously as by passing the oil charge and reagent into a reactor and heating under the desired conditions of temperature, pressure and time. The resulting mixture of iodine-containing tar, upgarded liquid products and gas is thereafter continuously separated. The upgraded product is fractionated to yield useful products and the residuum remaining is conducted to a hydrogenolysis unit where it undergoes hydrogenation in the presence of iodine which may inherently be contained in the residuum or added thereto as the aforementioned iodine-containing tar or iodine recovered therefrom.

Apparatus suitable for such an operation is illustrated diagrammatically in the appended drawing. Referring more particularly to the drawing, a hydrocarbon stock of high sulfur, nitrogen or metals content is pumped through conduit **1** and mixed with hydrogen, when desired, from conduit **2** and catalyst from conduit **3** before entering upgrading unit **4**. The catalyst may be fresh aqueous HI or I_2 pumped through line **24** or recycle catalyst, hereinafter described, pumped through line **25**. The preferable reaction conditions in the upgrading unit are: temperature 700–800° F., pressure 100–3000 p. s. i. g. and space velocity 0.2–4. Reaction product from the upgrading unit passes through conduit **5** to high pressure phase separator **6**. A heat exchanger, not shown, between vessels **4** and **6** may be desirably installed to cool the product. Gases from phase separator **6** are directed through line **7** into gas absorber **8** and any hydrogen contained therein is conducted through line **9** where it is met with make-up hydrogen from line **10** and compressed to 100–3000 p. s. i. g. before being recycled through upgrading unit **4**. Liquid product from phase separator **6** is passed through line **11** to fractionator **12**, along with the saturated absorber oil from line **13**. Gasoline and gas oil separated in fractionator **12** are removed through lines **35** and **36**, respectively. Tar from phase separator **6**, containing approximately 20–40% iodine, is removed through line **14** and may optionally be directed through line **15** for recycling to crude upgrading unit **4**, through line **16** to iodine recovery furnace **17**, or through line **18** for use as catalyst in hydrogenolysis unit **19**. The choice is dependent upon several factors, such as the amount of residuum being charged to the hydrogenolysis unit, and the accumulation of tar in the upgrading unit. Under normal operations, at least a portion of the tar will be directed through conduit **16** to iodine recovery furnace **17**. Regenerated iodine from furnace **17** may be passed through line **20** for use in upgrading unit **4** or through line **21** for use in hydrogenolysis unit **19**. Ash from furnace **17**, containing a high concentration of the trace metals, such as nickel and vanadium, is removed through conduit **22**.

In the second phase of the process, virgin residuum or other heavy stock is pumped through line **23** to hydrogenolysis unit **19**, along with hydrogen from line **26**, and fresh HI or I_2 from line **27** or recycle catalyst consisting of the tar produced in the above-described first stage

through line **28**. Residuum from the upgrading step is conducted through line **40**. The preferred reaction conditions in the hydrogenolysis unit are: temperature 800–950° F., pressure 500–1500 p. s. i. g. and space velocity 1–10. Product from hydrogenolysis unit **19** passes through line **29** to high pressure phase separator **30**. A heat exchanger, not shown, between vessels **19** and **30** may be desirably installed to cool the product. Gases from phase separator **30** are vented through line **31** to gas absorber **8**. Liquid product, containing suspended coke, is passed through line **32** to fractionator **37**. Unconverted residuum and coke separated in fractionator **37** are recycled through line **34** to hydrogenolysis unit **19**, with a portion being conducted to iodine recovery furnace **17** through line **33**. Gasoline and gas oil are removed from the fractionator through lines **38** and **39**, respectively. If the gasoline and gas oil are high in sulfur and nitrogen, which will depend on the residuum charged, the liquid product from phase separator **30** may be processed through upgrading unit **4**. Further processing of the gasoline and gas oil fractions, if desired or warranted, may be done in conventional equipment, such as stabilizers, reformers, caustic scrubbers, and catalytic cracking units.

The two stages of the above-described process are complementary and are more efficiently applied than the sum of the two steps separately, since (1) the residuum from the first step contains a catalytic amount of iodine, (2) the tar from the first step can be used as a catalyst in the second step and (3) only one unit for purification and pressuring of hydrogen and (4) only one unit for catalyst recovery are necessary. The combined process also affords considerable flexibility. Thus, a refinery handling a relatively small amount of high sulfur, high nitrogen crudes could upgrade such crude in the first step and accumulate enough catalytic tar for the hydrogenolysis of a large quantity of residuum obtained from the refinery's low sulfur, low nitrogen crudes. On the other hand, should the economics at a given time favor the use of residuum as fuel oil, the hydrogenolysis step would be used only on the residuum from the upgrading step and the catalytic tar from the upgrading step would be recycled or regenerated and the recovered iodine recycled.

The refining action obtained with the use of hydriodic acid, iodine, or solutions of iodine in hydriodic acid in accordance with the present process is unique in its effectiveness in comparison with the extent of refining obtained with other halides or hydrogen halide solutions. Thus, in comparable runs, aqueous HBr desulfurized a hydrocarbon stock 9 percent and aqueous HCl 28 percent under conditions at which aqueous HI desulfurized the identical stock 73 percent. The use of hydriodic acid for refining under conditions of the present invention accordingly provides an unexpectedly high selective removal of contaminant than either hydrofluoric or hydrochloric acid. In contrast to the present process, treatment of sulfur-containing stocks with HF, for example, throws out asphaltic materials which are higher in sulfur content than the balance of the stock and thus desulfurizes only in proportion to the amount of asphalt and sulfur content of the asphalt. Accordingly, with HF, poor yields and poor selectivity result while treatment with hydriodic acid or iodine in accordance with the above-described process affords high yields and good selectivity.

The following example will serve to illustrate the process of the invention without limiting the same:

A charge of crude oil contaminated with sulfur, nitrogen, and heavy metals is introduced to a stainless steel bomb together with approximately 30 pounds HI (as 55% aqueous solution) per barrel (315 pounds) of crude. Heat is applied and the temperature held at 700° F. for 2 hours, maximum pressure being 1400 p. s. i. g. At the end of this period, the heat is turned off and the bomb allowed to cool to room temperature.

The resulting product is separated into a gas, liquid upgraded product, and tar. The liquid product in turn is separated by fractionation into gasoline, gas oil, and residuum. The comparative amounts and properties of the various fractions are as follows:

	After Treatment	Crude Charge
Vol. percent recovery (including light ends)	91–95	
Wt. percent of hydrocarbon chg. to dry gas	4–8	
Wt. percent of hydrocarbon chg. to solids	4–9	
Whole liquid product:		
Specific gravity	0.8586	0.9065
API gravity	33.3	24.6
Bromine No.	15.0	14
Carbon residue (Conradson)	2.02	4.8
Percent Sulfur	0.25	1.21
Percent Nitrogen	0.16	0.49
Nickel, p. p. m.	0.1	47
Vanadium, p. p. m.	0.3	52
Iron, p. p. m.	0.7	28
Fractionated Product:		
Gasoline (410°F.), vol. percent liquid product	38	21
Specific gravity	0.8035	0.7958
API gravity	44.6	46.3
Percent Sulfur	0.055	0.21
Percent Nitrogen	0.02	0.02
Percent Iodine	Nil	
Gas Oil (410–750°F.), vol. percent liquid product	48	38
Specific gravity	0.9082	0.8939
API gravity	24.3	26.8
Bromine No.	11.7	15.0
Aniline No., °F.	107.6	137
Percent Sulfur	0.31	0.91
Percent Nitrogen	0.08	0.30
Percent Iodine	0.05	
Residuum (750°F.), vol. percent liquid product	14	41
Specific gravity at 77°F.	0.9885	1.0011
Percent Sulfur	0.49	1.81
Percent Nitrogen	0.33	0.78
Percent Iodine	0.18	
Total Tar Phase:		
Wt. percent of hydrocarbon charge	20–25	
Percent Iodine	25–35	

The total tar is conducted to an iodine recovery furnace and burned in air, yielding approximately 0.6 weight per cent of ash based on the tar, which, according to emission spectrographic analysis, consists of major amounts (over 10% by weight) of vanadium, nickel, and iron, and a minor amount (1–10% by weight) of copper.

The iodine recovered from the iodine recovery furnace is used as a catalyst in a hydrogenolysis unit in the amount of about 0.3 percent by weight of a charge of the residuum obtained as described above and boiling above about 750° F. Hydrogen in the amount of 2200 cubic feet per barrel of charge is introduced. The reaction conditions involve a temperature of 850° F., a pressure of 1200 p. s. i. g. and a space velocity of 4.

The resulting products of hydrogenolysis are separated by fractionation to yield 21 volume percent of 400° F. end point gasoline, 52 volume percent of 400–750° F. gas oil, 28 volume percent of residuum boiling above 750° F., 3 weight percent of dry gas, and 1 weight percent of coke.

Hydrogen consumption is 650 cubic feet per barrel, excess hydrogen being recycled. The residuum boiling above 750° F. may likewise be recycled to yield additional gasoline and gas oil.

The end products of the process are thus gasoline, gas oil, and an ash high in trace metal content. The yield of gasoline and gas oil from low grade crudes and residua is high and the quality as concerns the presence of non-hydrocarbons is good.

We claim:

1. A process for upgrading a hydrocarbon oil containing sulfur, nitrogen, and heavy metal contaminant, which comprises contacting said oil at a temperature between about 500 and about 850° F. and a pressure between about 100 and 3000 p. s. i. g. with a reagent selected from the group consisting of iodine, hydriodic acid, and mixtures thereof, effecting phase separation of the resulting gaseous, liquid and tarry products, fractionating said liquid product to yield gasoline, gas oil, and a residuum, contacting said residuum with hydrogen in the presence

of the aforementioned tarry product at a temperature between about 750° F. and about 1000° F. and a pressure between about 200 and about 3000 p. s. i. g., effecting phase separation of the products of such treatment into a gas and liquid, fractionating said latter liquid to yield gasoline, gas oil, and a second residuum, and recycling said second residuum to further treatment with hydrogen as aforesaid.

2. A process for desulfurizing and upgrading a sulfur containing hydrocarbon oil, which comprises contacting said oil at a temperature between about 700 and about 800° F. and a pressure between about 100 and about 3000 p. s. i. g. with between about 0.1 and about 30 percent by weight of a reagent selected from the group consisting of iodine, hydriodic acid, and mixtures thereof, effecting phase separation of the resulting gaseous, liquid and tarry products, fractionating said liquid product to yield gasoline, gas oil, and a residuum, contacting said residuum with hydrogen in the presence of at least a portion of the aforementioned tarry product at a temperature between about 800 and about 950° F. and a pressure between about 500 and about 1500 p. s. i. g., effecting phase separation of the products of such treatment into a gas and liquid, fractionating said latter liquid to yield gasoline, gas oil, and a second residuum, and recycling said second residuum to further treatment with hydrogen as aforesaid.

3. A process for upgrading low grade crude petroleum oil and treating a high boiling petroleum residuum, which comprises contacting said low grade crude petroleum oil at a temperature between about 500 and about 850° F. and a pressure between about 100 and about 3000 p. s. i. g. with about 0.1 to about 30 percent by weight of a reagent selected from the group consisting of iodine, hydriodic acid, and mixtures thereof, effecting phase separation of the resulting gaseous, liquid and tarry products, fractionating said liquid product to yield gasoline, gas oil, and a residuum, mixing said residuum with other high boiling petroleum residuum, contacting the resulting residuum mixture with hydrogen in the presence of between about 0.5 and about 25 percent by weight of the aforementioned tarry product at a temperature between about 750° F. and about 1000° F. and a pressure between about 200 and about 3000 p. s. i. g., effecting phase separation of the products of such treatment into a gas and liquid, fractionating said latter liquid to yield gasoline, gas oil, and a residuum, and recycling said residuum to further treatment with hydrogen as aforesaid.

4. A process for upgrading a low grade hydrocarbon oil, which comprises contacting said oil at a temperature between about 700 and about 800° F. and a pressure between about 100 and about 3000 p. s. i. g. with a reagent selected from the group consisting of iodine, hydriodic acid, and mixtures thereof, effecting phase separation of the resulting gaseous, liquid and iodine-rich tarry products, burning said tarry product to recover iodine therefrom, fractionating said liquid product to yield gasoline, gas

oil, and a residuum, contacting said residuum with hydrogen in the presence of the aforementioned recovered iodine at a temperature between about 800 and about 950° F. and a pressure between about 500 and about 1500 p. s. i. g., effecting phase separation of the products of such treatment into a gas and liquid, fractionating said latter liquid to yield gasoline, gas oil, and a second residuum, and recycling said second residuum to further treatment with hydrogen as aforesaid.

5. A process for desulfurizing and upgrading a sulfur containing hydrocarbon oil, which comprises contacting said oil with hydrogen at a temperature between about 500 and about 850° F. and a pressure between about 100 and about 3000 p. s. i. g. with about 0.1 and about 30 percent by weight of iodine, effecting phase separation of the resulting gaseous, liquid and tarry products, removing hydrogen from said gaseous product, and recycling the same to further contact with said oil, fractionating said liquid product to yield gasoline, gas oil, and a residuum, contacting said residuum with hydrogen in the presence of the aforementioned tarry product at a temperature between about 750° F. and about 1000° F. and a pressure between about 200 and about 3000 p. s. i. g., effecting phase separation of the products of such treatment into a gas and liquid, removing hydrogen from said gas product, and recycling such hydrogen to contact with the initial oil charge, fractionating the liquid product to yield gasoline, gas oil, and a residuum, and recycling said residuum for further treatment with said tarry product and hydrogen as aforesaid.

6. A process for upgrading a low grade hydrocarbon oil, which comprises contacting said oil at a temperature between about 500 and about 850° F. and a pressure between about 100 and about 3000 p. s. i. g. with between about 0.1 and about 30 percent by weight of a reagent selected from the group consisting of iodine, hydriodic acid and mixtures thereof, effecting phase separation of the resulting gaseous, liquid and iodine-rich tarry products, fractionating said liquid product to yield gasoline, gas oil, and a residuum containing at least 0.1 percent by weight of iodine, contacting said residuum with hydrogen at a temperature between about 750° F. and 1000° F. and a pressure between about 200 and about 3000 p. s. i. g., effecting phase separation of the products of such treatment into a gas and liquid, fractionating said later liquid to yield gasoline, gas oil, and a second residuum, and recycling said second residuum to further treatment with hydrogen as aforesaid.

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