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2,909,476

UPGRADING OF CRUDE PETROLEUM OIL

Filed Dec. 13, 1954

2 Sheets-Sheet 1

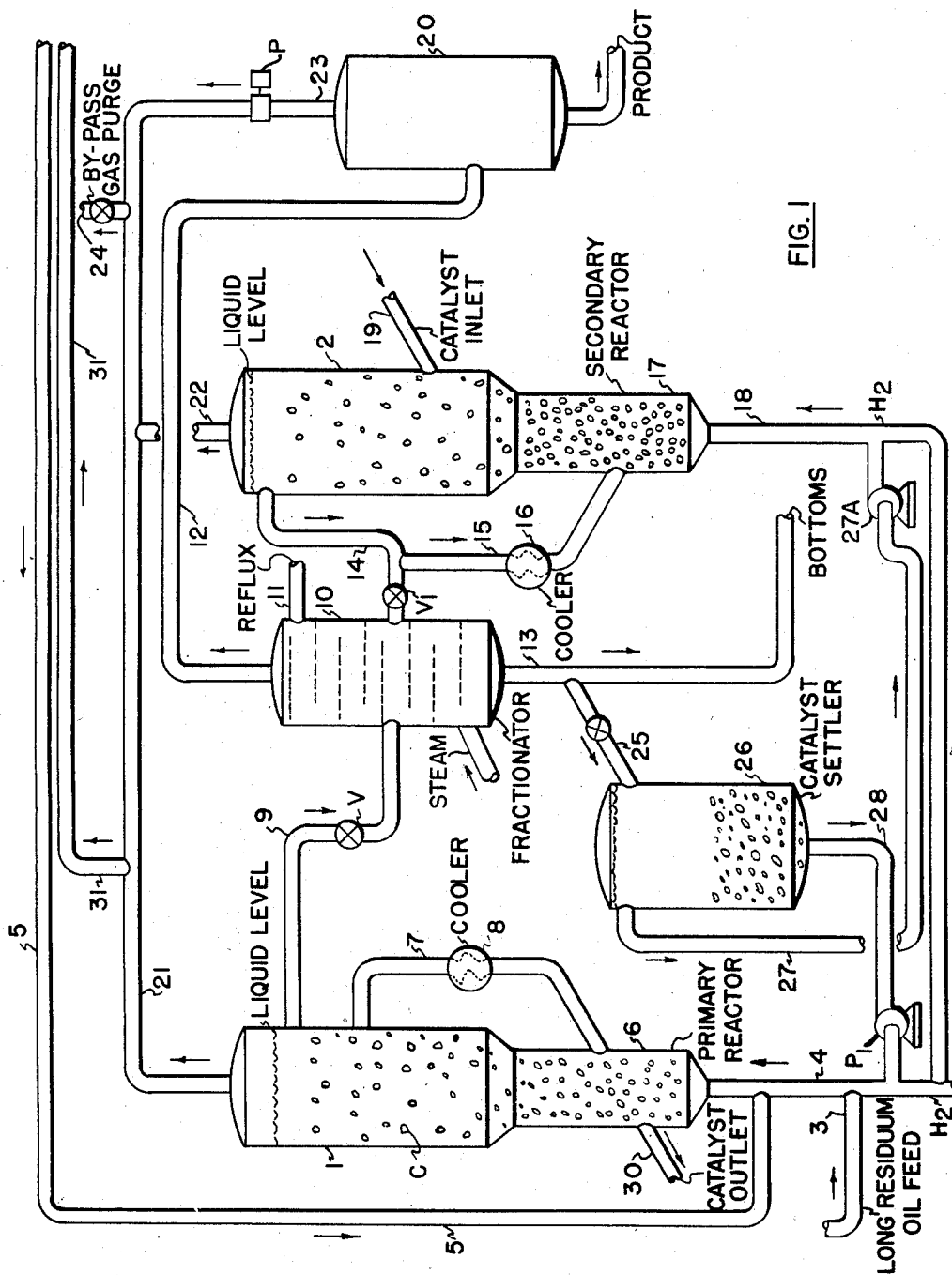


FIG. 1

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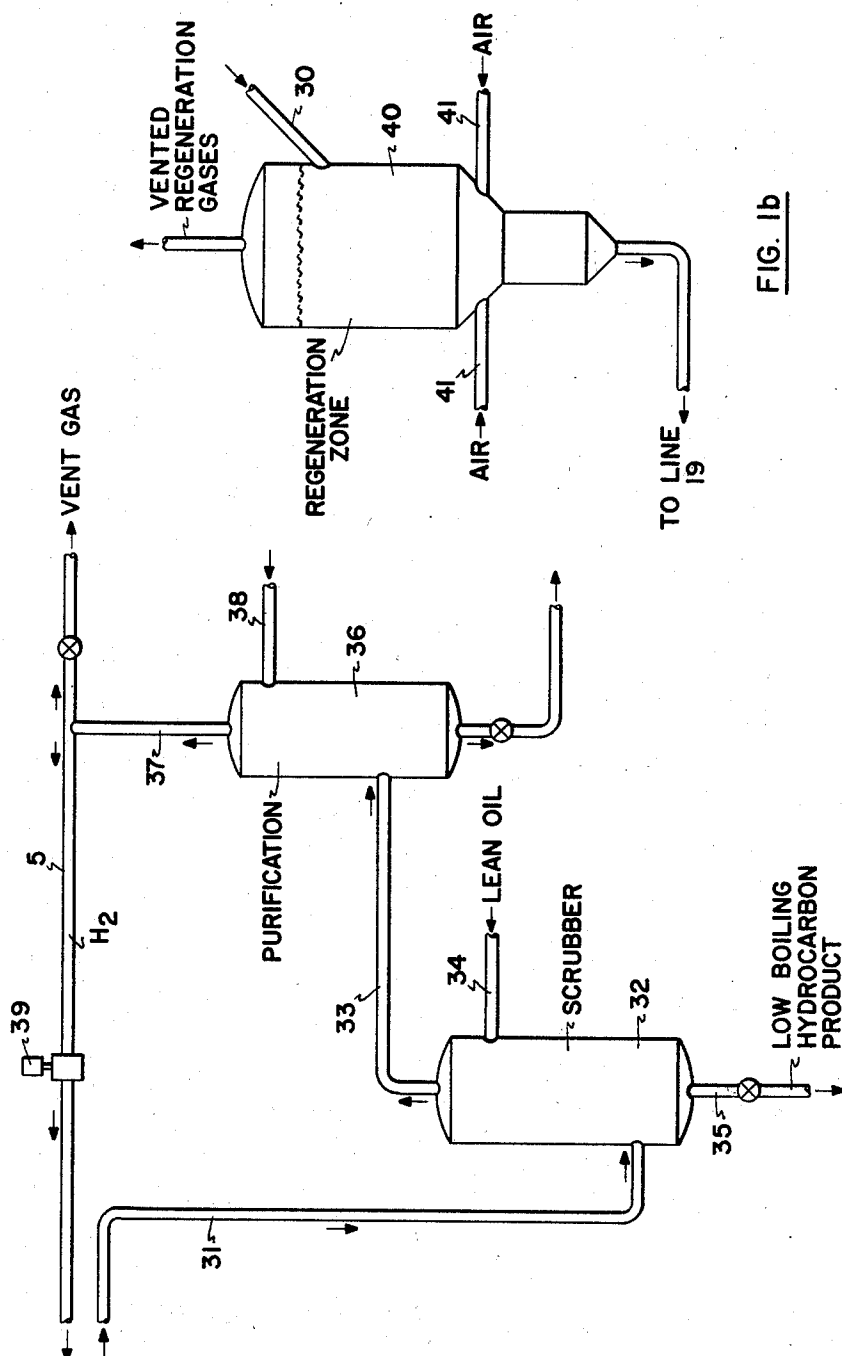


FIG. 1a

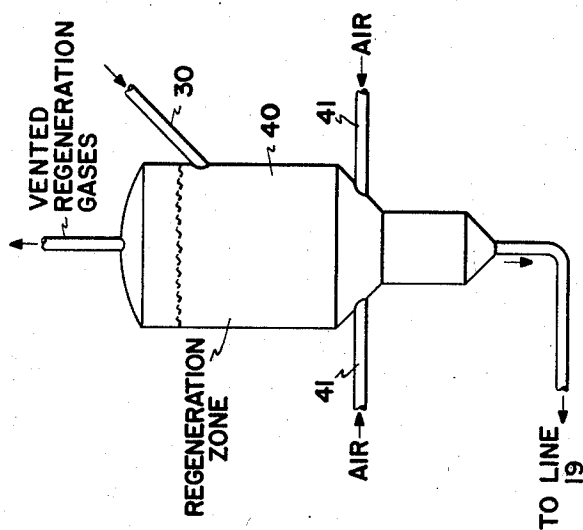


FIG. 1b

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2,909,476

UPGRADING OF CRUDE PETROLEUM OIL

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Application December 13, 1954, Serial No. 474,745

8 Claims. (Cl. 208—59)

The present invention relates to the upgrading of hydrocarbon oils. More particularly, the present invention relates to the hydrogenation or hydrocracking of heavy carbon oils to form, primarily, heating and gas oil as products, which also includes desulfurization of the crude, to remove coke-forming constituents, to remove metals and their salts contained in the original feed oil, and otherwise to upgrade the crude hydrocarbon oil.

In inventor's copending application Serial No. 401,633, filed December 31, 1953, there is disclosed and claimed a one vessel system for hydrogenating crude oil in a slurry liquid phase hydrogenation employing a solid catalyst.

The present invention relates to a two vessel or two stage operation in which a crude oil having an A.P.I. gravity of about, say, 15° is subject to hydrogenation in the presence of a hydrogenation catalyst, the operation being carried out in slurry phase, and the process being characterized in that a maximum amount of heating oils and gas oils are produced with a minimum of hydrocarbons boiling in the gasoline boiling range. In the first stage of the present process, the oil is treated with hydrogen in the presence of a hydrogenation catalyst under desulfurization and mild hydrogenation conditions. The product of this first stage is subjected to fractional distillation, and products boiling lower than 900°–1000° F. are separated from material boiling above 900°–1000° F., which latter material is then subjected to the influence of hydrogen in the presence of a hydrogenation catalyst under destructive hydrogenation conditions to form a substantial quantity of additional gas oil, which gas oil is a good catalytic cracking feed stock from which high quality gasoline may be produced by catalytic cracking the gas oil and also to produce diesel oil and a heating oil.

The prior art contains numerous proposals for upgrading heavy bottoms to form gasoline and gas oil for cracking to form cracked gasoline. One of these prior proposals involves what is known as coking of heavy petroleum oil bottoms to produce normally liquid products of lower boiling range, including gas oil and gasoline. The coking of heavy bottoms does not result, ordinarily, in the production of good gas oil, since the gas oil thus produced contains substantial quantities of polycyclic aromatics in a condensed nucleus which, when cracked, cause the formation of unduly large amounts of coke on the catalyst when they are used as a feed stock in a catalytic cracking operation. Another drawback to the coking operation is that it does not ordinarily result in the removal of any substantial amount of sulfur so that the product may contain undesirable amounts of sulfur.

In brief compass, the present invention involves, as previously indicated, a catalyst-slurry hydrogenation process which may be operated continuously to hydrogenate

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destructively hydrocarbon oils to form products of increased value. Since the process is a catalytic operation, means are provided for separating the catalyst from the products of hydrogenation, regenerating the catalyst with an oxygen-containing gas to remove carbon and other contaminating deposits, and also includes treatment of the catalyst, following normal regeneration, with a treating agent, such as diluted aqua regia to effect a redistribution of the hydrogenation component of the catalyst. Any good hydrogenation catalyst may be used, but cobalt molybdate or molybdenum oxide carried on an alumina of high surface area are preferred. However, the hydrogenation component of the catalyst may also be the oxides or the sulfides, supported on a carrier, or unsupported, of metals of the IV, V, VI and VIII groups of the periodic system. For instance, a catalyst that may be used with good results is one containing unsupported nickel sulfide and tungsten sulfide. As indicated, however, any recognized hydrogenation catalyst may be employed. A catalyst with 0.1 to 1.0% platinum on an alumina made by first reacting aluminum with an alcohol in the presence of a small amount of mercury, hydrolyzing and heating to yield an eta form of alumina may be used.

In the accompanying drawing there is depicted, diagrammatically, in Figures 1, 1a and 1b, an apparatus or system in which a preferred modification of the present invention may be carried into effect.

Referring in detail to the drawing, it will be noted that there is therein depicted two vessels 1 and 2, vessel 1 being a primary reactor wherein feed is desulfurized and partially destructively hydrogenated, while in vessel 2 a portion of the product from vessel 1, namely, that boiling above, say, about 900° F. and obtained from the fractional distillation column 10 as bottoms, is subjected to more severe hydrogenation in said vessel 2. A topped or residual petroleum oil feed in line 3 is admixed with hydrogen from line 4 and preheated in a furnace (not shown) and this heated mixture is mixed with recycled hydrogen from line 5, whereupon the said mixture is charged into the bottom portion 6 of primary reactor 1. It will be noted that reactors 1 and 2 are provided with expanded upper portions. In the case of reactor 1, the oil has an upper level, as indicated in the drawing, and it also contains distributed therethrough a powdered catalyst C. The mixture of oil and hydrogen passes upwardly through the lower portion of reactor 1 into the upper expanded portion and under conditions of temperature, pressure and residence time; more fully set forth hereinafter, desulfurization and a partial destructive hydrogenation of the oil feed occurs. The upper expanded portion of vessel 1 serves as a settling chamber wherein, due to the decreased velocity of the vapors and oil flowing therethrough, the catalyst tends to settle towards the lower portion of the reactor, which is more restricted in cross-sectional area. A product is withdrawn from vessel 1 through pipe 9, controlled by a pressure reducing valve V and charged to fractional distillation column 10. Steam may be added to the bottom of column 10 to aid in the distillation. As usual, the fractional distillation column is provided with re-boiling means (not shown) and also with reflux means (not shown). There is recovered overhead from vessel 1 gasiform material through line 21, and this gasiform material is treated in a manner more fully explained hereinafter. A portion of this gasiform material in line 21 may be rejected from the system through line 24. It is to be noted that a portion of the oil in reactor 1 is withdrawn from the system through line 7, passed through a cooler 8 and thence charged to the lower portion of reactor 1, the

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purpose of this, of course, is to control temperature by preventing over-heating of the oil in reactor 1. Overhead from distillation column 10, hydrocarbon vapors and hydrogen gas, are recovered through line 12 and delivered to a separation drum 20. The product is recovered as bottoms from separation drum 20 while volatile hydrocarbons and hydrogen are recovered overhead via line 23, a compressor P in line 23 serving to increase the pressure of the gasiform material in said line to that in line 21.

Referring again to fractional distillation column 10, a bottoms portion is removed through line 13 and a portion of this bottoms is charged to a settler 26. The catalyst settles to the bottom of 26, is withdrawn through line 28 in the form of a slurry and charged to line 4 for return to reactor 1. From an upper portion of settler 26, oil substantially free of catalyst is withdrawn through line 27 and pumped by 27A to line 18, wherein it is mixed with hydrogen and charged to the lower section 17 of reactor 2.

In reactor 2, the oil flows upwardly admixed with hydrogen from the lower section 17 to the upper expanded section and therein under conditions of temperature, pressure and residence time more fully set forth hereinafter, the oil undergoes further destructive hydrogenation. Gasiform material is recovered overhead from reactor 2 via line 22 and charged into line 21 and processed with the gasiform material from reactor 1 in a manner subsequently to be described. The treated oil is recovered from an upper portion of reactor 2 via line 14, carrying a pressure reducing valve V₁ and charged to fractionator 10 where it is subjected to fractional distillation, together with the product from reactor 1. A portion of the oil in line 14 is passed via line 15 through a cooler 16 and returned to the bottom portion of reactor 2, the cooled oil serving to control the temperature in reactor 2. It will be noted that fresh catalyst may be added to reactor 2, via line 19. Excess catalyst in reactor 2 passes through line 14, fractionator 10, line 25, catalyst settler 26, line 28 and line 4 to reactor 1 where it is used as a partially deactivated catalyst.

Now, referring to the gasiform material in line 31, the same is charged to a scrubber 32 (Fig. 1a), where it is treated with a lean oil added for the purpose of removing normally liquid hydrocarbons from the material in line 31 containing hydrogen, some liquid hydrocarbons and C₁-C₄ hydrocarbons. The gasiform material substantially freed of hydrocarbons to the extent that the hydrogen purity is 80-95%, is withdrawn overhead from 32 via line 33 and charged to a second scrubber 36. A purifying liquid, such as an aqueous alkaline solution, e.g., ethanolamine in water, is charged to the top of scrubber 36, via line 38, and this material dissolves out of the hydrogen-containing gas substantially all of the impurities which consist mostly of H₂S and other sulfur compounds. Overhead from scrubber 36, there is recovered via line 37 the purified hydrogen-containing gas which is charged to line 5, thence passed through a compressor 39 and recycled to reactors 1 and 2, as previously indicated, for further use in the process. A portion of the gas in line 5 may be rejected from the system, as indicated in the drawing (see Fig. 1a).

Referring again to reactor 1, catalyst may be withdrawn from the bottom portion 6 of said reactor, via line 30 and delivered to a catalyst regeneration zone 40 (see Fig. 1b), where the catalyst is treated with a regeneration gas comprising air, oxygen, or diluted air supplied by line 41 to remove contaminating constituents formed thereon during the processing, which contaminating constituents include carbonaceous material and sulfur-containing bodies. The regenerated catalyst may be activated by treating with halogens or acids. The regenerated catalyst is then returned to the system at any convenient point such as via line 19 to reactor 2.

In order more fully to describe the present invention, the following operating conditions are set forth:

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Conditions in reactor 1

	Range	Preferred
Catalyst:		
Wt. Percent CoO.....	2-10	4-6
Wt. Percent MoO ₃	5-15	8-10
Temperature, °F.....	700-800	730-760
Pressure, p.s.i.....	400-2,000	800-1,200
Residence Time, Lbs. Oil per hr. per lb. of catalyst.....	0.5-5.0	1-2
Standard cubic feet of H ₂ per barrel of oil.....	500-5,000	1,000-2,000

Conditions in reactor 2

	Range	Preferred
Catalyst:		
Wt. Percent CoO on alumina.....	2-10	4-6
Wt. Percent MoO ₃ on alumina.....	5-15	8-10
Temperature, °F.....	750-900	800-825
Pressure, p.s.i.....	400-2,000	800-1,200
Residence Time, Lbs. Oil per hr. per lb. of catalyst.....	0.5-5.0	1-2
Standard cubic feet of H ₂ per barrel of oil.....	500-5,000	1,000-2,000

Conditions in fractionator 10

	Range	Preferred
Pressure, p.s.i. absolute.....	5-300	20-100
Steam added, parts per 100 parts overhead.....	0-100	10-50

In order to explain the invention more fully, the following specific example is set forth:

A West Texas residuum having an A.P.I. gravity of about 18°, also containing 2.50% by weight of sulfur, and 21.7 lbs. per thousand barrels of minerals, including iron, vanadium, nickel and the like, may be treated according to the present invention by processing it in the first stage of the foregoing described process to a temperature of about 740° F. in the presence of a powdered catalyst, having a particle size of from 200-400 mesh, the said catalyst consisting of 4 wt. percent of CoO and 9 wt. percent MoO₃ on 87 wt. percent of alumina. The catalyst may be distributed uniformly throughout the oil in a first reaction stage. About 1000 standard cubic feet of hydrogen per barrel of oil feed may be charged to the first stage of the reaction, the hydrogen having a concentration of about 85% by volume. A temperature of about 740° F. may be maintained in the said first stage and the pressure maintained in the first stage may be 800 p.s.i. The residence time of the oil in the first stage may be 2 lbs. of oil per hour per pound of catalyst in the reactor. The oil may be withdrawn and charged to a fractionator where it is subjected to fractional distillation while under a pressure of 100 p.s.i. with about 10 wt. percent steam on feed residuum added.

There may be taken overhead a product boiling in the range of from methane to 1000° F. The bottoms from the said fractionating column, having a boiling range of above about 1000° F. may be charged to a second stage reaction zone where it may be slurried with a portion of the same catalyst employed in the first stage. A temperature of 820° F. and a pressure of 800 p.s.i. may be maintained in the second stage. A hydrogen-containing gas of about 85% purity may be fed to the second reaction zone, the amount of said hydrogen being about 1000 standard cubic feet per barrel of oil. The oil may be permitted to remain resident under the conditions stated as determined by the space velocity of 1 lb. oil per hour per lb. of catalyst. A product may be withdrawn from the said second stage and charged to the said fractionating column where it is subjected to fractional distillation with the product of the first stage. The combined

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product from the stages may be subjected to distillation with the following results:

Inspection of feed in line 3

A.P.I. gravity	18
Sulfur content, wt. percent	2.50
Minerals content:	
V, p.t.b. ¹	5.2
Ni, p.t.b.	2.2
Fe, p.t.b.	14.3

Yields based on feed

Vol. percent of 0-400° F. material	16
Vol. percent of 430-650° F. material	32
Vol. percent of 650-1000° F. material	48
Vol. percent of 1000° F.+ material	6
C ₄ hydrocarbons, vol. percent	1.5
C ₃ - hydrocarbons, wt. percent	4.7
Wt. percent S in naphtha fraction	0.2
Wt. percent S in below fractions:	
430-650° F.	0.3
650-1000° F.	0.7
1000° F.+	2.7

¹ P.t.b.=lbs. of minerals per thousand barrels of oil.

To recapitulate briefly, the present invention comprises improvements in upgrading oils, particularly, heavy or high boiling crude oils, such as crudes having an A.P.I. gravity of 15° or higher by treating the said oil with hydrogen in the presence of a hydrogenation catalyst. The main purpose of the invention is to provide a maximum quantity of product boiling in the gas oil range, which oil is particularly suitable for feed stock in a catalytic cracking operation. Since those constituents of the oil which tend to produce coke, such as aromatics having a plurality of benzene rings in a condensed nucleus, such aromatics are at least partially converted to naphthenes, which naphthenes are excellent feed stock for catalytic cracking operation. The present process results in the removal of sulfur, this result being accomplished mainly in the first stage of the process. It also results in the production of valuable heating oils and diesel fuels, and furthermore, is characterized in that a minimum amount of naphtha is formed. The process does require extraneous hydrogen, but the amount of hydrogen is not excessive since 400-800 standard cubic feet of hydrogen per barrel of oil fed is sufficient to accomplish the foregoing results.

Another advantage of the present process is that the major portion of materials, such as iron, arsenic, common salt, and the like, which may be contained in the residuum, are eliminated so that when, for example, the gas oil is catalytically cracked, these materials are not present to contaminate or deactivate the catalyst. As to the catalysts employed in the processing, any good hydrogenation-dehydrogenation catalyst may be used, such as cobalt molybdate carried on alumina, molybdenum sulfide suitably supported, platinum group metals suitably supported, or a mixture of nickel and tungsten sulfides. Zinc aluminate carrying a hydrogenation-dehydrogenation component may be employed with good results. It is also desirable to include from 0.5-5 wt. percent silica in the catalyst base composition.

The present process may be operated continuously. The catalyst may be withdrawn and regenerated with air or other oxygen-containing gas. It is also advisable to include chlorine in the catalyst composition. In regenerating the catalyst, a slurry may be of catalyst and oil withdrawn from the first reactor and charged to a settler where it is permitted to remain quiescent until the major portion of the catalyst settles to the bottom of the settler. The supernatant oil is withdrawn and the concentrated slurry is filtered to separate it from the heavy oil. The catalyst may then be stripped with steam to remove adhering oil and then the stripped catalyst may be suspended in steam and charged to gas-solids separating device where the catalyst is in substantially dry

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form, separated from the carrier gas and formed into a suspension in a regeneration gas. This suspension may be conducted to a regeneration zone where the catalyst is formed into a dense fluidized bed and treated at temperatures of, say, 1000-1200° F. with an oxygen-containing gas to remove the catalyst contaminants. The catalyst treated in this conventional regeneration method may then be soaked in oxygen or air for an extended period of time, say, 24 hours at a temperature of 1050°-1200° F. This latter step need not be required after each conventional regeneration but may be employed when the catalyst is not fully reactivated by conventional regeneration. The catalyst not fully reactivated by conventional regeneration and soaking in oxygen or air may be treated with aqua regia at room temperature while in the form of a slurry. The effect of this treatment is to redisperse the active hydrogenation-dehydrogenation catalyst on the carrier and at the same time to reduce the crystalline size of the said hydrogenation-dehydrogenation component. The hydrogenation-dehydrogenation catalyst may increase in crystalline size to a value of, say, 150-250 A. units, in which state it may have a diminished activity. By treating with aqua regia, the catalyst is redissolved and redispersed on the carrier in a crystalline size, which is not greater than about 50 A. units, and this small sized catalyst possesses greater activity than a catalyst having a crystal size of 150-250 A. units. The method of reactivating the catalyst is described in detail in inventor's copending application Serial No. 401,633, filed December 31, 1953.

Many modifications of the present invention may be made by those who are familiar with the art.

What is claimed is:

1. A method of producing a substantial quantity of oil boiling in the range of from about 400°-1000° F. from a crude metals-containing oil having an API gravity of 15° or higher which comprises contacting said oil in a slurry with a hydrogen-containing gas in the presence of a partially deactivated hydrogenation catalyst in a first reactor zone operated under desulfurization and mild hydrogenation conditions of 400-2000 p.s.i.g. and 700°-760° F. to form a quantity of lower boiling range oils, removing products boiling lower than about 900°-1000° F., contacting the remaining heavy portion in a slurry in a second reaction zone with a hydrogen-containing gas in the presence of a freshly regenerated hydrogenation catalyst operated under destructive hydrogenation conditions of 400-2000 p.s.i.g. and 800°-900° F., whereby a substantial quantity of additional lower boiling oils is formed, maintaining the total amount of hydrogen consumed in both zones below 400 s.c.f./bbl., passing catalyst from the second reaction zone to the first reaction zone, from the first reaction zone to regeneration with an oxygen-containing gas, and from regeneration back to the second reaction zone and recovering a total product from the process which includes a substantial amount of gas oil.

2. The process as defined in claim 1 in which the products from the destructive hydrogenation second zone are fractionated to separate the products boiling below 900°-1000° F. from the higher boiling constituents and said higher boiling constituents are recycled to the destructive hydrogenation second zone.

3. A method of producing a substantial quantity of oil boiling in the range of from about 400°-1000° F. from a metals-containing crude oil having an API gravity of 15° or higher which comprises contacting said oil in a slurry with a hydrogen containing gas in the presence of a partially deactivated hydrogenation catalyst in a first reaction zone operated under hydrodesulfurization and mild hydrogenation conditions of 400-2000 p.s.i.g. and 700-760° F. to form a quantity of lower boiling range oils, removing by distillation products boiling lower than about 1000° F., contacting the remaining heavy portion in a slurry with a hydrogen-containing gas in the presence of

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a freshly regenerated hydrogenation catalyst in a second reaction zone operating under destructive hydrogenation conditions of 400–2000 p.s.i.g. and 800–900° F. whereby a substantial quantity of additional lower boiling oils is formed, maintaining the total amount of hydrogen consumed in both zones below 400 s.c.f./b. passing catalyst from the second reaction zone to the first reaction zone, from the first reaction zone to regeneration with an oxygen-containing gas, and from regeneration back to the second reaction zone and recovering a total product from the process which includes a substantial amount of gas oil.

4. The process of claim 3 in which the products from the hydrodesulfurization first zone are fractionated at a pressure of 5–300 p.s.i.g. to separate products boiling below 900–1000° F. from the higher boiling constituents, a portion of the higher boiling constituents are passed to the destructive hydrogenation second zone and the remainder of the high boiling constituents are recycled to the first desulfurization zone to control temperatures in said first zone.

5. The method set forth in claim 3 in which the catalyst is platinum carried on an active form of alumina.

6. The method set forth in claim 3 in which the material recovered from distillation boiling above about 1000° F. is partially rejected from the system, thus removing a substantial quantity of minerals contained in the original oil.

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7. The method set forth in claim 3 in which liquid oil is withdrawn from the hydrodesulfurizing step, cooled and returned to the said hydrodesulfurization step to control temperatures.

8. The method set forth in claim 3 in which liquid oil is withdrawn from the destructive hydrogenation step, cooled and returned to the said step to control temperatures.

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