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CONVERSION OF OIL RESIDUA TO LIGHTER HYDROCARBONS

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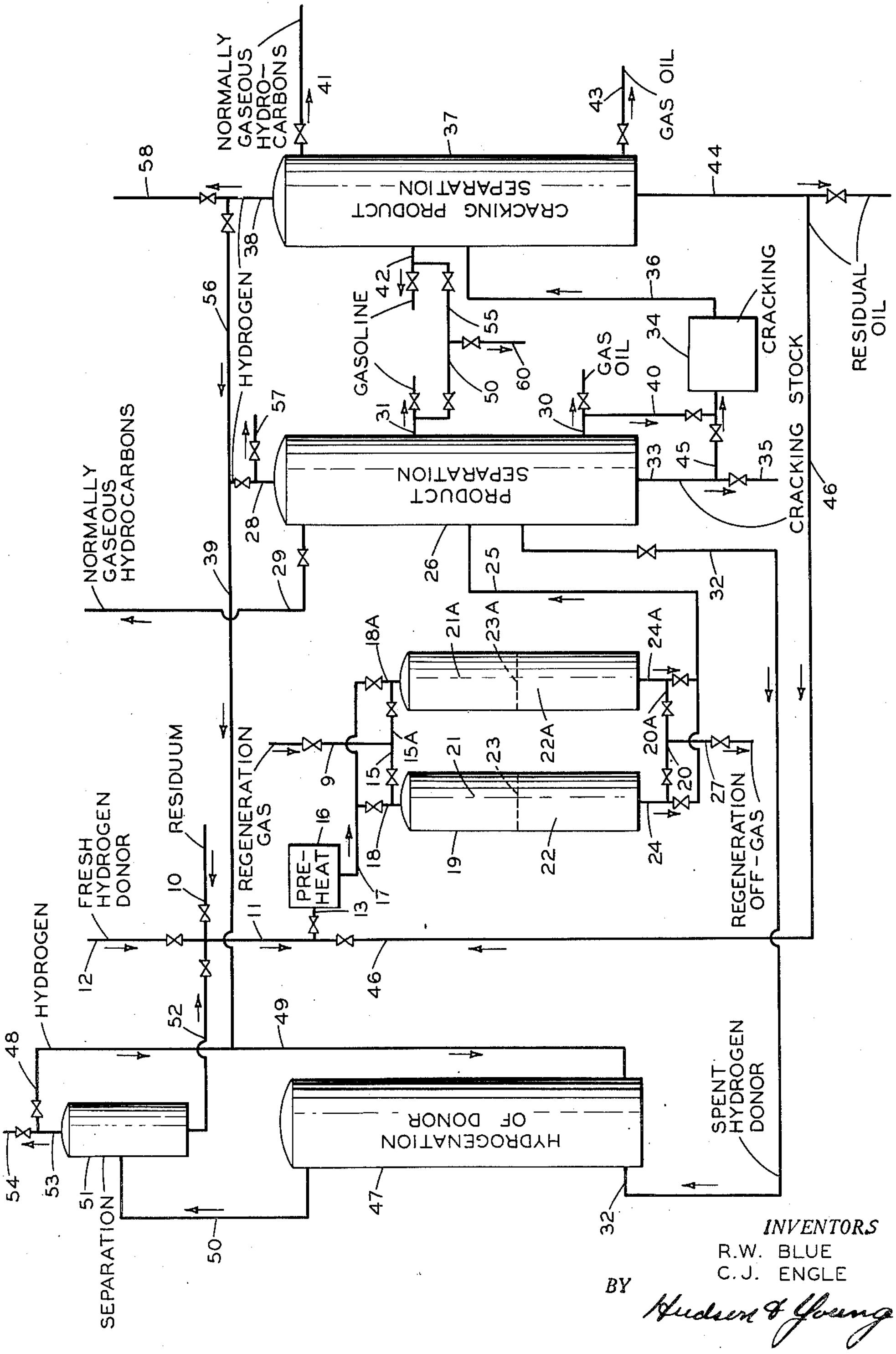

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CONVERSION OF OIL RESIDUA TO LIGHTER HYDROCARBONS

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This invention relates to the conversion of oil residuum stocks to lighter and more valuable hydrocarbons. In another embodiment this invention relates to the manufacture of feed stocks for hydrocarbon cracking.

Residuum oil stocks are non-distilled residual oils generally having a boiling range above about 700° F. and a gravity generally below about 25° API. Typical of such residuum stocks are topped crude, reduced crude, vacuum reduced crude, topped crude cracking residuum, and the like. These residuum materials contain high proportions of carbon to hydrogen, and when subjected to conventional cracking temperature conditions, form large deposits of coke. Accordingly, when attempting to crack oil residua, low yields of desired product are obtained, and short cracking periods are necessary together with time-consuming and expensive steps for removal of carbon-containing deposits from the conversion system.

Our invention is concerned with a process for the conversion of oil residua to lighter and more valuable hydrocarbons, wherein a residuum is first treated in contact with a plurality of catalysts in the presence of a hydrogen donor, and product from that treatment is subjected to conventional cracking.

An object of our invention is to provide for the conversion of oil residuum stocks to hydrocarbon cracking product.

Another object is to provide for the manufacture of hydrocarbon-cracking feed stocks from oil residua.

Another object is to provide a novel catalytic treatment for the conversion of a hydrocarbon oil residuum to lighter hydrocarbons, boiling in a range above about 400° F. and having especial utility as feed stock for hydrocarbon cracking.

Other objects will be apparent to those skilled in the art from the accompanying discussion and disclosure.

In accordance with one embodiment of our invention, an oil residuum is converted to lighter and more valuable hydrocarbons by first passing the residuum in contact with an olefin-forming catalyst under conditions of temperature, pressure and time, for forming olefins from the residuum, and then passing the resulting olefin-containing product in contact with a hydrogen transfer catalyst in the presence of a hydrogen donor, under similar conditions of time, temperature and pressure to those employed in the presence of the olefin-forming catalyst. Effluent from these catalytic reactions, is then distilled to produce a high-boiling fraction suitable for use as a hydrocarbon-cracking feed stock, a lower-boiling product containing material originally introduced into the hydrogen transfer zone, alone or together with any suitable materials formed during either or both of the catalytic steps above described, which upon non-destructive hydrogenation, will act as hydrogen donor, and a by-product gasoline fraction containing valuable isoparaffins. Material thus recovered is at least partially depleted of transferable hydrogen, and is hydrogenated and then recycled as hydrogen donor for reuse in the hydrogen transfer zone. Cracking feed stock thus recovered as product, is cracked in accordance with conventional methods, either catalytically or non-catalytically, to produce desired cracking product, particularly hydrocarbons boiling in the gasoline range.

In a preferred embodiment, we admix an oil residuum with hydrogen donor, preheat the resulting residuum-donor mixture and pass the preheated mixture through a bed of a first catalyst known to have high olefin-forming activity and low hydrogen transfer activity, under which conditions unsaturates are formed from the residuum in high yield. Effluent from the bed of olefin-forming catalyst, containing olefins and hydrogen donor, is then passed through a bed of a second catalyst known to have high hydrogen transfer activity under which conditions olefins present isomerize, and hydrogen is transferred to olefins present, including those isomerized, to form a product having a higher API gravity, a higher H/C ratio, and a lower boiling range, than that of the original untreated residuum, and being particularly suitable for conversion by conventional cracking methods to desired cracking product fractions, particularly gasoline fractions.

When referring herein to a hydrogen donor it is meant to include hydrogen donor materials added to the system with or without donor formed as product, in the presence of either or both of the olefin-forming and hydrogen transfer catalysts. Such materials, whether formed as product in the system, or added thereto from an outside source, contain combined hydrogen in an unstable state of combination at high temperatures, i. e. at the hydrogen transfer catalyst temperatures employed herein. When product from the olefin-forming step is treated in admixture with one of these donor compounds in the hydrogen transfer step, unstably combined hydrogen is transferred from that donor compound to olefins in contact therewith, bringing about their hydrogenation. Such a reaction is referred to herein as hydrogen transfer, the compound furnishing the hydrogen being referred to as a hydrogen donor, and the unsaturate thus hydrogenated being referred to as the hydrogen acceptor. Various well known hydrogen donors particularly well applied in the practice of our invention include such compounds as tetralin, decalin, naphthene product fractions, and the like.

We have found that various silica-containing materials are particularly well suited for use as olefin-forming catalysts and hydrogen transfer catalysts in the practice of our invention, an essential factor determining the choice of a catalyst for either use, being the silica content of the material selected. Silica-containing catalysts employed in the olefin-forming step of our process, necessarily contain not more than 25 weight per cent silica, often from 1 to 10%, whereas silica-containing catalysts employed in the hydrogen transfer step necessarily contain more than 25 weight per cent silica, often from 30 to 70 per cent.

Activated silica-containing natural clays and synthetic silica alumina-type catalysts are particularly representative of many catalysts that we can employ in the practice of our invention.

When referring herein to silica-alumina-type catalysts, we means not only to include synthetic silica-alumina, often preferred in the practice of our invention, particularly as a hydrogen transfer catalyst, but also other silica-metal oxide catalysts of similar nature but differing among themselves as to one or more specific properties and containing along with silica, an oxide of a metal selected from group IIIB or from group IVA of the periodic system. As listed in "Modern Inorganic Chemistry" by J. W. Mellor (Longmans Green & Co. (1939), revised and edited by G. D. Parkes) on page 118, group IIIB consists of boron, aluminum, gallium, indium, and thallium and group IVA consists of titanium, zirconium, hafnium, and thorium.

Silica-alumina type catalysts used in the practice of our invention can be prepared in any suitable manner. For example, well known precipitation methods can be employed in the preparation of silica-alumina type catalysts suitable herein for use either as hydrogen transfer catalyst or an olefin-forming catalyst. Atypical coprecipitation procedure comprises forming a silica-metal oxide hydrogel by adding an acid or an acid salt to a solution of an alkali metal silicate and a salt of a metal of the desired metal oxide, as for example, sodium aluminate; washing the hydrogel free of soluble material; and drying the resulting gel.

A procedure often employed in the preparation of a silica-alumina type catalyst particularly suitable as a hydrogen transfer catalyst, comprises forming a hydrous silica gel from an alkali metal silicate and an acid, washing soluble material from the gel, treating or activating the gel with an aqueous solution of a suitable metal salt and subsequently washing and drying the treated material. In this manner a part of the metal presumably in the form of a hydrous oxide or loose hydroxide compound formed by hydrolysis is selectively adsorbed by the hydrous silica, and is not removed by subsequent washing.

The proportions of silica and metal oxide of silica-metal oxide catalysts prepared by precipitation methods can be varied over a broad range, containing as for example, from 1 to 99 per cent silica as desired, dependent on the selected initial concentrations in the hydrogel-forming mixture of the salts to be precipitated. Silica-alumina type catalysts formed by activation of a hydrous silica gel will contain generally from 90 to 99 per cent silica, more often from 94 to 99 per cent.

Among various natural silica-containing clays particularly suitable as an olefin-forming catalyst is an activated bauxite having an iron oxide content, generally below 3 to 4 per cent by weight, and activated by being heated under controlled conditions (500 to about 800° F.) to provide improved porosity and improved adsorption characteristics. Low iron content is secured in part by selection and in part by heating followed by magnetic separation of any magnetic iron oxide particles. Low iron bauxite of the type discussed herein contains generally from 1 to 10 per cent by weight of silica, more often from about 2 to 7 per cent.

Among various natural occurring silica-containing clays well suited for use as a hydrogen transfer catalyst in our process is that known as "Super Filtrol," described in an article by Davidson et al. at pages R-318 to R-321 of "National Petroleum News," issue of July 7, 1943. This material occurs in nature—before activation—as montmorillonite, which is believed to have the ideal formula $Al_2Si_4O_{10}(OH)_2nH_2O$, and an actual formula corresponding to

$$MgO.Al_2O_3SiO_2.nH_2O$$

since in nature the ideal formula is not realized due to substitutions. The natural montmorillonite clay has a crystalline rather than an amorphous or gel structure, as exemplied by silica gel. One apparently typical substitution in the formula of the product as found in nature is partial replacement of aluminum by magnesium. This montmorillonite mutation does not appear to be haphazard, but characteristically every sixth aluminum ion is apparently supplanted by a magnesium ion, and this replacement of a trivalent cation (aluminum) by a divalent cation (magnesium) is believed to give rise to a deficiency in positive charge. The crystal lattice of the ideal montmorillonite unit crystal cell is characterized by a layer configuration, and each layer is believed to consist of four sheets of oxygen, between the outer sheets of which in the tetrahedral position are located the silicon atoms; in the octahedral position are the aluminum atoms, and in the same oxygen sheets which form the boundaries of the octahedrals are the hydroxyl ions. The deficiency in positive charge caused in the neutral product by the replacement of tht trivalent cation by the divalent cation causes the lattice to become negatively charged, and in order to neutralize this charge, various types of cations are adsorbed on the crystal protruding into the water of hydration space between the layers of montmorillonite. The cations, being exposed, are subject to mass action effects and are readily replaceable, thus giving rise to the phenomenon of base exchange which is a characteristic of the substituted montmorillonite.

The raw montmorillonite clay is commonly classified as a non-swelling bentonite and is sometimes referred to as a subbentonite.

Modification of the raw montmorillonite to provide a suitable catalyst for the present invention is effected by activation. The most common form of activation is by means of an acid, and in treating a magnesium substituted montmorillonite in the raw form for use as a catalyst by acid activation, impurities are removed with attendant increase in effective catalytic surface, and also exchangeable ions are replaced by hydrogen: i. e., the surface cations originally present in a magnesium substituted montmorillonite lattice are replaced by hydrogen ions as a result of the activation. Thus, the activated material may be termed a magnesium substituted hydrogen montmorillonite. A further effect of the acid treatment in activating the montmorillonite clay may well be to dissolve a disproportionate amount of alumina, thus increasing the percentage of magnesia. A sample of the activated montmorillonite clay is characterized by the following analysis:

Magnesia	percent by weight	4.9
Alumina	percent by weight	14.4
Water	percent by weight	21.9
Silica		Remainder

It is to be understood that although we prefer silica-containing catalysts such as those of the types discussed above for use as catalysts in carrying out the process of our invention, our invention is not to be limited to the use of these catalysts as other catalysts can be employed in carrying out our process. For example alumina combined with from 1 to 10 per cent of its weight of thoria, titania or zirconia or with not more than 10 per cent of a mixture of one or more of these oxides is suitable for use as an olefin-forming catalyst; and zirconia combined with from 10 to 40 per cent of its weight of alumina, magnesia, or thoria or with not more than 40 per cent of a mixture of these oxides is suitable for use as a hydrogen transfer catalyst. Silica containing from 10–40 per cent of its weight of magnesia is a suitable hydrogen transfer catalyst.

Understanding of the invention will be facilitated upon reference to the attached diagrammatic flow sheet illustrative of a preferred embodiment of our invention. It is to be understood that the flow sheet is diagrammatic only, and can be altered in many respects by those skilled in the art and yet remain within the intended scope of our invention.

With reference to the drawing, a naphthenic topped crude, having a gravity of from 0 to 25° API and boiling in a range above 700° F., is passed from line **10** through line **11** into line **13**, in admixture with a hydrogen donor material from line **12** as for example, decalin, with or without hydrogen donor product formed as described hereafter, introduced from line **52**. Oil is admitted into line **11** in a volume ratio to hydrogen donor within the limits of about 1:1 to 10:1, a more preferable range of volume ratio being within the limits of from 2:1 to 5:1. The specific proportions of hydrogen donor and oil in line **11** are dependent to a large extent upon the specific feed stock employed, i. e. the greater the naphthenic or asphaltic content, the greater the proportion of hydrogen donor employed. The oil-hydrogen donor mixture in line **11** is passed through line **13** into preheating zone **16** and heated therein to a temperature generally within the limits of from 700 to 950° F., more preferably from about 750 to 850° F. At these temperatures in these ranges, some carbonaceous materials may precipitate from the oil-hydrogen donor mixture in which case preheater zone **16** may be advantageously adapted to remove such precipitated material. In one form, preheater **16** can comprise a plurality of gas fired coils through at least one but not all of which the oil-donor mixture from line **13** is passed and heated in indirect exchange relation with the heat source. Then after carbonaceous material deposits in the first coil or coils, oil and donor can be passed through one or more of the remaining coils, while simultaneously removing the carbonaceous deposits from the first coil or coils, i. e. a cyclic type of heating-carbon-removal operation wherein the oil mixture is continuously heated to the desired temperature and withdrawn through line **17**. In another form, zone **16** can be a conventional pebble heater apparatus into which oil-donor mixture from line **13** is introduced and heated in direct heat exchange relation with a moving contiguous pebble mass previously heated to a requisite temperature for effecting the necessary transfer of heat to the oil-donor mixture. Any carbonaceous materials precipitating from the oil settle on the pebble surfaces or become entrained with the moving pebble mass, being thus continuously removed from the preheating system to provide for continuously preheating the oil-hydrogen donor mixture.

Heated oil-donor mixture is passed from line **17** through line **18** into catalyst zone **19** containing catalysts **21** and **22** disposed in tandem relation to each other, separated as indicated by demarcation line **23**. Upper disposed catalyst **21** is an olefin-forming catalyst of the type already described, having low activity for effecting hydrogen transfer and hydrocarbon conversion, and being active in promoting formation of olefins from oil introduced into contact therewith from line **18**. Catalyst **22** disposed in tandem below catalyst **21** is an active hydrogen-transfer catalyst of the type already discussed and promotes transfer of hydrogen from the hydrogen donor to olefins in contact therewith, at the same time promoting some olefin isomerization and the formation of highly branched paraffin hydrocarbons, many of which boil in the gasoline boiling range.

We prefer to maintain the volume of the olefin-forming catalyst **21** in zone **19** in a ratio to the volume of catalyst **22** therein, within the limits of about 2.5:1 to 1:1.

Oil-donor mixture from line **18** is introduced into zone **19** at a space velocity within the range of from 0.5 to 5 volumes per total volume of catalysts **21** and **22** in zone **19** per hour, more preferably at such a space velocity within the limits of from 1 to 3.

Pressure in chamber **19** can be selected from within the limits of atmospheric to 85 p. s. i. g., more preferably from 10 to 45 p. s. i. g. An initial pressure drop across chamber **19** may be about 5 to 15 p. s. i. during the flow of oil and hydrogen donor therethrough, dependent to a large extent upon the selected space velocity.

The tandem relation of catalysts **21** and **22**, in chamber **19** is particularly advantageous, for the reason that the olefin-forming reaction is endothermic whereas the hydrogen-transfer reaction is exothermic; accordingly heat lost to the endothermic olefin-forming reaction is to a large extent made up by a supply of exothermic heat liberated from the hydrogen transfer reaction. Operating in this manner heat is conserved, and the net temperature drop across chamber **19** is generally not more than about 10 to 25° F.

In chamber **19**, oil in contact with catalyst **21** is converted to olefins together with a concomitant degradation of some of the oil to carbonaceous catalyst deposits low in hydrogen. The resulting olefin-rich product in contact with catalyst **22** accepts hydrogen from the hydrogen donor, enhancing the oil in hydrogen content and rendering it suitable for further conversion to lower boiling hydrocarbons.

Some isomerization occurs in the presence of catalyst **22** to form low boiling isoolefins which are then hydrogenated to form saturated isocompounds, many of which are in the gasoline boiling range. Other products formed in chamber **19** include various gas oil fractions, and naphthene fractions themselves capable of acting as hydrogen donors in the presence of catalyst **22**. Effluents are withdrawn from chamber **19** through line **24** and passed through line **25** to product separation zone **26**, which is preferably a fractionation system comprising various storage vessels, fractionators, and the like not individually illustrated.

Removal of degradation product, i. e. carbonaceous materials from the surface of catalysts in chamber **19**, can be facilitated if desired by employing a cyclic type catalyst regeneration-oil conversion operation to maintain continuous conversion of the oil. This can be done by switching flow of oil-hydrogen donor from line **18** to line **18***a* when it is desired to remove carbonaceous deposits from the surfaces of catalysts in zone **19**, passing the diverted oil-donor stream through chamber **19***a* containing catalysts **21***a* and **22***a*, and withdrawing effluent from chamber **19***a* through line **24***a* and passing same to separator **26** through line **25**; it being understood that conditions of time, pressure, space velocity, and the like in chamber **19***a* are the same as those in chamber **19**, and that catalysts **21***a* and **22***a* are the same respectively as catalysts **21** and **22**.

During the time that oil-hydrogen donor flow is directed through chamber **19***a*, oxygen-containing regeneration gas containing from about 1 to about 10 volume per cent free oxygen, generally from about 3 to 6 per cent, can be passed through chamber **19** from line **9** through line **15**, whereby at the existing temperature in chamber **19**, carbon-containing materials on the catalyst surfaces are burned to form gaseous carbon oxides and are removed in the regeneration off gas, withdrawn through lines **24**, **20** and **27**. Catalyst renegeration gas is passed through chamber **19** at a space velocity to maintain a regeneration temperature therein within the limits preferably of from 900 to 1200° F., although higher or lower space velocities can be employed if desired. Such cyclic type operation provides for continuously forming product alternately in chambers **19** and **19***a* and at the same time alternately regenerating catalyst in these chambers.

From product separation zone **26** is withdrawn hydrogen of at least 50 per cent purity and preferably from 70 to 90 per cent, through line **28**, normally gaseous hydrocarbons through line **29**, gasoline through line **31**, hydrogen donor material deficient in hydrogen as a result of transfer of hydrogen to olefins in chamber **19**, through line **32**, and hydrocarbons boiling above the gasoline range particularly suitable for conversion by cracking to gasoline-containing cracking product through line **33**. Material withdrawn through line **32** can be a fraction of a narrow boiling range containing the hydrogen donor originally introduced into the system from line **12** or more preferably a product fraction including the originally added hydrogen donor together with other naphthene product compounds, capable of serving as a hydrogen donor in chamber **19**, or **19***a* in the presence of catalysts **22** or **22***a*; the latter product fraction boiling preferably in a range within the limits of about 130 to 225° C.

Hydrocarbons boiling above the gasoline boiling range in line **33** are hydrogen-rich materials, having an API gravity generally of from 30 to 50°, and formed as a chief product of olefin-forming and hydrogen transfer effected in chambers **19** or **19***a*. Product in line **33** can be subjected to either catalytic or non-catalytic cracking to produce gasoline in high yield together with relatively low yields of normally gaseous hydrocarbons, and hydrocarbons boiling above the gasoline range. Product in line **33** is passed into cracking zone through line **45** and cracked preferably non-catalytically at a temperature generally of from about 900 to about 1000° F. Conventional conditions of cracking time, pressure and the like can be selected as desired, as for example a pressure within the limits of about 0.5 to 2 atmospheres and a time within the limits of from about 0.01 to 1 second or higher.

In some instances it may be desired to recover a cracking stock from zone **26**, very similar to the material in line **33** but free of heavy ends therein. This can be done in accordance with a separate embodiment of our invention by withdrawing a desired gas oil fraction from zone **26** through line **30**. Gas oil in line **30** can be passed to cracking zone **34** and cracked, preferably in the presence of a catalyst, under cracking conditions of temperature, time, pressure and the like, in about the same ranges as those above described, although somewhat less severe, particularly when employing a catalyst. A suitable cracking catalyst can be selected from a large number of well known cracking catalysts. Effluents from cracking zone **34** contain typical cracking products as hydrogen, normally gaseous hydrocarbons, together with hydrocarbons boiling in the gasoline range and relatively small yields of gas oils. Total product is withdrawn from zone **34** through line **36** and passed into cracking product separation system **37** comprising various storage vessels, fractionators and other auxiliary equipment not specifically illustrated, for separating product from zone **34** into desired fractions. From separation zone **37** is withdrawn hydrogen of at least 50 per cent purity, generally from 70 to 90 per cent, through line **38**, normally gaseous hydrocarbons through line **41**, hydrocarbons boiling in the gasoline range through line **42**, a gas oil fraction through line **43**, and a residual oil product through line **44**, which if desired, can be recycled from line **44** through line **46** to line **11**.

Gasoline in line **42** is of somewhat lower quality than gasoline in line **31** by virtue of the material in line **31** containing isomerization and hydrogen transfer product formed in zone **19** or **19***a*, as already discussed. However, a blend of these two fractions can be made by passing gasoline from each of lines **31** and **42** through lines **50** and **55** respectively into line **60** to form a resulting blend of quality superior to that of gasoline obtained by conventional cracking alone. The resulting gasoline blend can be withdrawn from line **60**.

Hydrogen donor material in line **32**, at least partially depleted of transferable hydrogen, is contacted in hydrogenation chamber **47** with hydrogen introduced into chamber **47** from line **49**, containing hydrogen from sources described hereafter. The hydrogenation in chamber **47** is conducted in the presence of any well known hydrogenation catalyst particularly sulfactive hydrogenation catalysts such as molybdenum disulfide, copper chromite, or the like, and nickel catalysts as nickel chromite or Raney nickel or the like, when the donor to be hydrogenated is free of catalyst-poisonous compounds, particularly sulfur. The hydrogenation of donor in zone 47 is generally conducted at a temperature of from about 400 to 600° F. at a space velocity of from about 1 to 10 volumes of liquid hydrogen-donor per catalyst volume per hour. Hydrogenation pressures employed in zone 47 are usually sufficient to maintain the donor material in liquid phase, and are generally from 10 to 50 p. s. i. g., although higher pressures as from 100 to 1000 p. s. i. g. are often employed. Total effluent is withdrawn from hydrogenation zone **47** through line **50** and passed to separation zone **51** wherein hydrogen donor, no longer deficient in transferable hydrogen, is separated from hydrogen, often by flash distillation. Saturated donor is withdrawn from zone **51** through line **52** and recycled to line **11** as already discussed. Hydrogen of at least 50 per cent purity separated in zone **51**, is withdrawn through line **53** and recycled in whole or in part as desired from line **53**, through line **48** to line **49**. Any hydrogen in line **53** not recycled through line **48** is withdrawn through line **54**. Hydrogen in line **28** is recycled in whole or part as desired, to line **49** through line **39**. Any hydrogen in line **28** not recycled to line **49** is withdrawn through line **57**. Hydrogen in line **38** is recycled in whole or in part as desired through lines **56** and **39** to line **49**. Any hydrogen in line **38** not recycled to line **49** is withdrawn from line **38** through line **58**.

In the foregoing discussion of the attached diagrammatic figure certain apparatus such as pumps, surge tanks, accumulators, valves, and the like, have not been shown in the drawing, for the purpose of convenience and clarity. Obviously such modifications of the present invention may be practiced without departing from the scope of the invention.

In summary, our invention provides for the conversion of heavy hydrocarbon oil residua to more valuable and lighter hydrocarbons by a series of steps involving (1) admixing the heavy residuum oil with a hydrogen donor material; (2) charging the resulting oil-hydrogen donor mixture into a conversion unit containing two catalyst beds in tandem, the catalyst first contacted by the oil-donor mixture being an olefin forming catalyst and the second catalyst contacted being an active hydrogen transfer catalyst; (3) distilling effluent from the conversion unit to obtain a high boiling fraction suitable for use as hydrocarbon cracking feed stock, and a lower boiling fraction suitable for use as donor material in step (1); and (4) cracking the feed stock thus produced and recovering selected cracking product fractions, particularly hydrocarbons boiling in the gasoline range.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of the foregoing disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

We claim:

1. A process for the conversion of a hydrocarbon oil residuum to a hydrocarbon cracking stock boiling in a range lower than that of said residuum, comprising passing an admixture of such a residuum having a gravity within the limits of 0 to 25° API and a boiling range above 700° F. and a naphthene hydrocarbon as a hydrogen donor material, containing oil in a volume ratio to said hydrogen donor within the limits of 1:1 to 10:1 at a temperature within the limits of 700 to 950° F., into a reaction zone containing a first bed of a granular alumina-metal oxide catalyst selected from the group consisting of alumina combined with from 1 to 10 per cent of its weight of at least one metal oxide selected from the group consisting of thoria, titania, and zirconia, and an alumina-silica containing not more than 25 weight per cent silica and selected from the group consisting of a synthetic silica-alumina type catalyst and a natural occurring clay, disposed in tandem relation with a second bed of granular metal oxide catalyst selected from the group consisting of zirconia combined with from 10 to 40 per cent of its weight of at least one oxide selected from the group consisting of alumina, magnesia and thoria, and a silica-alumina containing more than 25 weight per cent silica and selected from the group consisting of a synthetic silica-alumina type catalyst and a natural occurring clay, the volume ratio of said first bed to said second bed being within the limits of 2.5:1 to 1:1, passing said oil-hydrogen donor admixture through said reaction zone through said first bed and then through said second bed at a space velocity within the limits of 0.5 to 5 volumes per volume of total catalyst in said reaction zone per hour, separating liquid product from reaction zone effluent suitable for hydrocarbon cracking, and recovering said liquid product thus separated as a product of the process.

2. The process of claim 1 wherein said first bed of granular catalyst is a bauxite containing not more than 4 per cent iron oxide.

3. The process of claim 1 wherein said second bed of granular catalyst is a synthetic silica-alumina type catalyst containing from 25 to 99 per cent silica.

4. The process of claim 1 wherein said second bed of granular catalyst is a magnesium substituted hydrogen montmorillonite.

5. The process of claim 1 wherein said first bed of granular catalyst is a synthetic silica-alumina type catalyst containing from 1 to 25 weight per cent silica.

6. A process for the conversion of a hydrocarbon oil residuum to lighter hydrocarbons, comprising passing a hydrocarbon oil residuum having a gravity within the limits of 0 to 25 API and a boiling range above 700° F. in admixture with decalin in a volume ratio of said oil to said decalin within the limits of 1:1 to 10:1 to a preheating zone and therein heating the oil-decalin mixture to a temperature within the limits of 700 to 950° F., passing the heated oil-decalin mixture into a catalytic reaction zone at a space velocity of 0.5 to 5 volumes per volume of total catalyst in said catalytic reaction zone first through a first bed of granular olefin-forming catalyst disposed in tandem with a second bed of granular hydrogen transfer catalyst and then through said hydrogen transfer catalyst, the volume ratio of said first bed to said second bed being within the limits of 2.5:1 to 1:1, said olefin-forming catalyst comprising an activated bauxite containing not more than 4 per cent iron oxide and said hydrogen transfer catalyst comprising a synthetic silica-alumina containing from 25 to 99 per cent by weight silica, passing effluent from said reaction zone to a product separation zone and therein separating liquid product from said effluent suitable for hydrocarbon cracking and a hydrogen donor fraction containing decalin at least partially deficient in transferable hydrogen, passing said liquid product thus recovered to a cracking

zone and therein cracking same, passing said hydrogen donor fraction thus recovered to a hydrogenation zone and therein hydogenating same, thereby regenerating said donor, recycling regenerated donor to said preheating zone in admixture with said hydrocarbon oil residuum and decalin, and recovering product from said cracking.

7. The process of claim 6 wherein said hydrogen donor passed to said hydrogenation zone is a napthene fraction boiling in a range within the limits of 130 to 225° C., and said cracking is catalytic.

8. The process of claim 6 wherein said liquid product passed to cracking is bottoms product from fractionation of catalytic reaction zone effluent.

9. The process of claim 7 wherein said donor deficient in transferable hydrogen is regenerated by hydrogenation in the presence of a hydrogenation catalyst at a temperature within the limits of from 400 to 600° F.

10. A process for the conversion of a hydrocarbon oil residuum to a hydrocarbon cracking stock boiling in a range lower than that of said residuum, comprising passing an admixture of such a residuum having a gravity within the range of 0 to 25° API and a boiling range above 700° F. and a naphthene hydrocarbon as a hydrogen donor material, containing oil in a volume ratio to said hydrogen donor within the range of 1:1 to 10:1 at a temperature within the range of 700 to 950° F. through a bed of granular alumina-metal oxide catalyst selected from the group consisting of alumina combined with from 1 to 10 percent of its weight of at least one metal oxide selected from the group consisting of thoria, titania, and zirconia, and an alumina-silica containing not more than 25 weight per cent silica and selected from the group consisting of a synthetic silica-alumina type catalyst and a natural occurring clay, withdrawing hot effluent from the zone of said catalyst and directly passing same through a bed of granular metal oxide catalyst selected from the group consisting of zirconia combined with from 10 to 40 per cent of its weight of at least one oxide selected from the group consisting of alumina, magnesia and thoria, and a silica-alumina containing more than 25 weight per cent silica and selected from the group consisting of a synthetic silica-alumina type catalyst and a natural occurring clay, the ratio of the volume of the first said catalyst to the volume of the second said catalyst being within the limits of 2.5:1 to 1:1, passing said oil-hydrogen donor mixture through the first said catalyst bed and through the second said catalyst bed at a space velocity within the range of 0.5 to 5 volumes per volume of total catalyst in said beds per hour, separating liquid product from the effluent from the zone of the last said catalyst suitable for hydrocarbon cracking, and recovering said liquid product thus separated as a product of the process.

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