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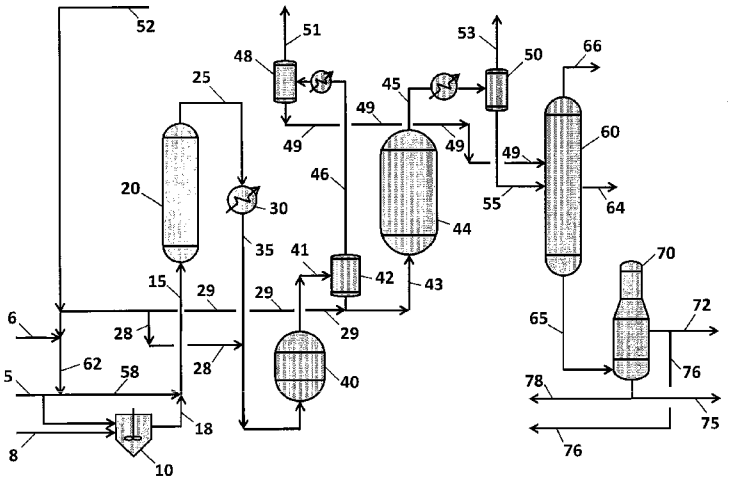
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(54) Title: TWO-ZONE, CLOSE-COUPLED, DUAL-CATALYTIC HEAVY OIL HYDROCONVERSION PROCESS UTILIZING IMPROVED HYDROTREATING



(57) Abstract: A process for hydroconversion of heavy oil feedstocks that effectively controls asphaltene condensation by utilization of a combination of dispersed coal, dispersed catalyst using a two- zone close-coupled thermo-catalytic reactor/catalytic-hydrotreating reactor configuration. The process converts heavy hydrocarbonaceous feed-stocks, a significant portion of which boils above 540°C, to high yields of high quality products boiling below 540°C. The first zone of the process is a thermo-catalytic zone, in which the feedstock is substantially converted to lower boiling products. The product of the thermo-catalytic zone is cooled somewhat and passed directly, without substantial loss of hydrogen partial pressure, into a catalytic-hydrotreating zone, where the thermo-catalytic zone effluent is hydrotreated to produce hydrotreated products suitable for further treatment into transportation fuels and other products. The catalytic-hydrotreating zone is comprised of two sub-zones, one before and one after a hot separator. The first treating sub-zone accomplishes the immediate hydrogenation of unstable molecules. The hot separator removes light products and gases providing a heavy product stream that can be more efficiently treated with higher purity recycle and make-up hydrogen-rich streams.

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Two-zone, Close-coupled, Dual-catalytic Heavy Oil Hydroconversion Process Utilizing Improved Hydrotreating

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 61/601,344, filed 21 February 2012.

BACKGROUND OF THE INVENTION

[0002] Field of The Invention

The present invention relates to a process for the hydroconversion of heavy hydrocarbonaceous fractions of petroleum. In particular, it relates to a close-coupled two-zone process -- a thermo-catalytic zone followed by a catalytic-hydrotreatment zone -- for converting petroleum heavy oils that provides improved effectiveness for high conversion and control of condensation reactions to produce stable high-quality products.

[0003] Background

Increasingly, petroleum refiners find a need to make use of heavier or poorer quality crude feedstocks in their processing. As that need increases, the need also grows to process the fractions of those poorer feedstock's that boil at elevated temperatures, particularly those fractions boiling above 540°C. High conversions to stable, high quality products are desirable in order to avoid producing significant quantities of lower value fuel oil. Delayed coking, the refiner's traditional solution for converting heavy oils to liquid products, has become less attractive because of the low conversion to liquid products and the relatively low value of the coke byproduct. Higher liquid conversions can be achieved with conventional ebullated bed technologies. But these technologies, even with enhancements such as solvent de-asphalting, suffer limitations due to the instability of the fuel oil product and refractive nature of the products – making further upgrading difficult.

[0004] Severe process conditions are required in order to achieve high conversions. These conditions, while producing desirable lighter fractions, can also produce thermally cracked fragments and unstable asphaltenes that form mesophase masses. Unless controlled, the cracked fragments undergo condensation reactions to form undesirable polycyclic molecules which tend

to be unstable and difficult to process into desirable products. Along with the mesophase masses, they can also lead to coke formation.

[0005] The key to high conversion and product quality is the management of the asphaltenes which are produced at severe operating conditions. Current approaches have focused on slurry reactor technology utilizing sophisticated dispersed catalyst systems, in some cases employing molybdenum. These technologies tend to have high investment and operating costs and, in some cases, product quality remains an issue. Many of these processes also have difficulties if the metals content of the feedstock is high.

[0006] Various processes for the conversion of heavy hydrocarbonaceous fractions, particularly multi-stage conversion processes, include those described in U.S. Pat. No. 4,761,220, Beret, et al.; U.S. Pat. No. 4,564,439, Kuehler, et al.; U.S. Pat. No. 4,330,393, Rosenthal, et al.; U.S. Pat. No. 4,422,922, Rosenthal, et al.; U.S. Pat. No. 4,354,920, Rosenthal, et al; U.S. Pat. No. 4,391,699, Rosenthal, et al., U.S Patent No. 4,851,107, Kretschmar , et al., U.S. Pat. App. No. 2008/0156693 A1, Okui, et al., U.S. Patent No. 6,660,157, Que Guohe et al.

SUMMARY

[0007] The present invention is, in broad scope, a process for converting the portion of heavy oil feedstock boiling above 540°C, to produce high yields of high quality products boiling below 540°C. Compared to existing processes, the products are reduced in heteroatom content, reduced in condensed-ring molecule content and are more readily processed to finished fuels.

[0008] The process comprises introducing a mixture comprising heavy oil feedstock, coal and dispersed catalyst particles, into a thermo-catalytic zone in the presence of hydrogen and operated at elevated temperature and pressure. The feedstock, coal, and dispersed catalyst mixture is introduced into the thermo-catalytic zone under conditions sufficient to convert a significant amount of hydrocarbons in the feedstock boiling above 540°C to hydrocarbons boiling below 540°C. Substantially all of the thermo-catalytic zone gaseous, liquid and solid effluent is passed directly, in a close-coupled manner, into a second zone for catalytic-hydrotreating. Inter-zone cooling is used to reduce the temperature of the process stream from the first zone to a process temperature suitable for hydrotreatment in the second zone. In the second zone, the first zone effluent is contacted with hydrotreating catalysts under hydrotreating conditions sufficient to stabilize the heavy product by capping free radical reactions. The treated effluent is then flashed

to remove light products and gases and the heavy solids-containing liquid phase from the separator is further treated to reduce the quantity of and improve the quality of the heavy liquid products. The effluent from this second hydrotreating zone is recovered.

[0009] In a broad form the present invention relates to a process for conversion of heavy oils to produce lower boiling hydrocarbon products comprising; dispersing finely divided coal and catalyst in a heavy oil feedstock, heating and passing the dispersed mixture together with hydrogen to a first reaction zone, the product of which is reduced in temperature and passed to a second reaction zone having a supported hydrotreating catalyst and wherein the first and second reaction zone are close-coupled, operated at elevated temperature and pressure, the first reaction zone is comprised of thermo-catalytic reactor(s) and the second reaction zone is comprised of at least two catalytic-hydrotreating reactors in series with a hot separator between reactors that removes light products and gases and passes its liquid/solid phase to the downstream catalytic-hydrotreating reactors; and recovering the product of the catalytic-hydrotreating zone. The surprising benefit of removing light products and gases after the first reactor of the catalytic hydrotreating zone, is that the full stabilization of the products from the thermocatalytic reactor takes place rapidly in the first reactor of the catalytic hydrotreating zone, allowing the volume of the downstream reactor(s) of the catalytic-hydrotreating zone to be reduced in size, due to the lower amount of reactant in the system. Further, the reaction conditions may be tailored to the needs of the heavy hydrotreated stream directed to the downstream hydrotreatment reactor(s). Furthermore the withdrawn light gases may be replenished by a stream with high hydrogen content for a more effective reaction, possibly also allowing a different choice of catalyst in the downstream reactors of the catalytic-hydrotreating zone.

[0010] In a further embodiment substantially all effluent from the thermo-catalytic zone is passed into the first reactor of the catalytic-hydrotreating zone.

[0011] In a further embodiment the dispersed catalysts are the oxides or sulfides of metals chosen from the Groups VIb, VIIb and VIIIb metals.

[0012] In a further embodiment the dispersed catalysts are either a synthetic catalyst or a naturally occurring material.

[0013] In a further embodiment the dispersed catalyst is limonite, a naturally occurring iron oxide/hydroxide mineral.

[0014] In a further embodiment the temperature of said first-reaction thermo-catalytic zone is maintained within a range of 400°C to 480°C.

[0015] In a further embodiment the temperature of said thermo-catalytic zone is maintained within a range of 425°C to 470°C.

[0016] In a further embodiment the products from the catalytic-hydrotreating reactor(s) are separated into gaseous, liquid and a liquid/solid bottom fractions and wherein a portion of the liquid and/or liquid/solid fraction bottoms is recycled back to the feed system.

[0017] In a further embodiment the products from the catalytic-hydrotreating zone are separated into gaseous and liquid/solid bottom fractions and wherein a portion of a gaseous fraction containing hydrogen is recycled to the hydrotreating reaction zone.

[0018] In a further embodiment the products from the catalytic-hydrotreating zone are separated into gaseous and liquid/solid bottom fractions and wherein a portion of a gaseous fraction containing hydrogen is recycled to thermo-catalytic reaction zone.

[0019] In a further embodiment the temperature of the catalytic-hydrotreating zone is 340°C to 425°C.

[0020] In a further embodiment the temperature of the catalytic-hydrotreating zone is preferably 360°C to 415°C.

[0021] In a further embodiment the amount of heavy oil in the feedstock is converted to hydrocarbons boiling below 540°C is at least 50 percent.

[0022] In a further embodiment the amount of heavy oil in the feedstock is converted to hydrocarbons boiling below 540°C is preferably at least 90 percent.

[0023] In a further embodiment said heavy oil feedstock is selected from the group consisting of crude petroleum, topped crude petroleum, reduced crudes, petroleum residua from atmospheric or vacuum distillations, solvent deasphalted tars and oils, heavy hydrocarbonaceous liquids derived from coal, bitumen, or coal tar pitches.

[0024] In a further embodiment said heavy oil feedstock is co-processed with oils such as VGO, Coker Gas Oil, and/or FCC Cycle Oil.

[0025] In a further embodiment the concentration of coal dispersed in the feed to the thermo-catalytic zone is between 0.5 and 40 percent by weight.

[0026] In a further embodiment the concentration of coal dispersed in feed to the thermo-catalytic zone is between 0.5 to 20 percent by weight.

[0027] In a further embodiment the concentration of coal dispersed in the feed to the thermo-catalytic zone is about 3 to 10 percent by weight.

[0028] In a further embodiment the amount of dispersed catalyst in the feed to the thermo-catalytic zone is from about 0.1 to 5 percent by weight.

[0029] In a further embodiment the residence time of the material in the thermo-catalytic reaction zone is from about 0.5 to 3 hours.

[0030] In a further embodiment the total residence time of material in the catalytic-hydrotreating zone is from about 0.3 to 4 hours and the residence time in the zone that is upstream of the hot separator is 0.1 to 1 hour.

[0031] In a further embodiment the supported catalyst in said catalytic hydrotreating zone is maintained in fixed, ebullated, or moving bed(s) within the reaction zone.

[0032] In a further embodiment the process is maintained at a hydrogen partial pressure from about 35 atmospheres to 300 atmospheres.

[0033] In a further embodiment said metal contaminants in the feedstock include nickel, vanadium, and iron and where they are substantially removed from the feedstock in the thermo-catalytic zone.

DESCRIPTION OF THE DRAWINGS

[0034] Figure 1 is a schematic flow diagram of the process of the present invention.

DETAILED DESCRIPTION

[0035] This invention is a process for hydroconversion of heavy oil feedstocks that effectively controls asphaltene condensation by utilization of a combination of dispersed coal, dispersed catalyst, and a two-zone close-coupled thermo-catalytic reactors/catalytic-hydrotreating reactors configuration. It converts heavy hydrocarbonaceous feed-stocks, a significant portion of which boils above 540°C, to high yields of high quality products boiling below 540°C.

[0036] The process is a two-zone, close-coupled process, the first zone of which comprises a thermo-catalytic zone, wherein the feedstock is substantially converted to lower boiling products. The product of the thermo-catalytic zone is cooled somewhat and passed directly, without substantial loss of hydrogen partial pressure, into a catalytic-hydrotreating zone, where the thermo-catalytic zone effluent is hydrotreated to produce hydrotreated products suitable for further

treatment into transportation fuels and other products. The catalytic-hydrotreating zone is comprised of two sub-zones, one before and one after a hot separator. The first treating sub-zone accomplishes the immediate hydrogenation of unstable molecules. The hot separator removes light products and gases providing a heavy product stream that can be more efficiently treated with higher purity recycle and make-up hydrogen-rich streams.

[0037] In the thermo-catalytic zone, the dispersed catalyst catalyzes the hydrogenation of thermally cracked fragments and stabilizes them, thus preventing condensation reactions. The dispersed catalyst also hydrogenates coal liquids, which coal liquids in a non-catalytic process also act to hydrogenate a portion of thermally cracked fragments by donating hydrogen to them. The coal liquids also act to solubilize asphaltenes and asphaltenes precursors and inhibit the formation of mesophase masses. Close-coupled catalytic-hydrotreating plays a key role in promptly stabilizing remaining thermally cracked fragments from the first zone, hydrogenating products, removing heteroatoms and effecting some further molecular weight reduction. The unconverted coal and coal ash sequester the metals in the feedstock in the thermo-catalytic zone which results in substantial reduction of metals fouling of the supported hydrotreating catalyst in the first catalytic-hydrotreating sub-zone.

[0038] Thermo-catalytic cracking tends to produce unstable products. This can lead to both the fouling of downstream equipment and the production of poor quality products. Placing the lower temperature catalytic-hydrotreating zone directly after the thermo-catalytic zone (in a single high pressure loop) assures the prompt saturation of unstable molecules that were created in the thermo-catalytic zone. In contrast to conventional processing, which places separations steps such as distillation after the thermo-catalytic zone, and does not directly pass the liquids and liquids/solids from the thermo-catalytic zone to a catalytic-hydrotreating zone, this prompt stabilization significantly reduces the polymerization of unstable molecules to form undesirable asphaltenes. Thus, the zones are "close-coupled". Close-coupled then, refers to the connective relationship between these zones. The pressure between the thermo-catalytic zone and the catalytic-hydrotreating zone is maintained such that there is no substantial loss of hydrogen partial pressure. In a close-coupled system also, there is no separation of solids from liquids as the thermo-catalytic effluent passes from one zone to the other, and there is no more cooling and reheating than necessary. However, it is necessary to cool the first-zone effluent by passing it

through a cooling zone prior to the second zone. This cooling does not affect the close-coupled nature of the system. The cooling zone will typically contain a heat exchanger or similar means, whereby the effluent from the thermo-catalytic zone is cooled to a temperature between 340°C and 425°C in order to reach a temperature suitable for hydrotreating without excessive fouling of the hydrotreating catalyst in the catalytic-hydrotreater. Some cooling may also be effected by the addition of a fresh, cold, hydrogen-rich stream.

[0039] Feedstocks finding particular use within the scope of this invention are heavy hydrocarbonaceous feedstocks, at least 30 volume percent, preferably 50 volume percent of which boils above 540°C. Examples of typical feedstocks include crude petroleum, topped crude petroleum, reduced crudes, petroleum residua from atmospheric or vacuum distillations, solvent deasphalted tars and oils, and heavy hydrocarbonaceous liquids including residua derived from coal, bitumen, or coal tar pitches. Herein, these feedstocks are referred to as "heavy oil". Other feedstocks such as vacuum gas oils, coker gas oils, and FCC cycle oils may also be favorably co-processed with these heavy oils.

[0040] The process of the invention may be more fully understood by reference to Figure 1 that illustrates the invention. Heavy oil feedstock (hydrocarbonaceous feedstocks, a significant portion of which boils above 540°C) enters the process by line 5. Some portion of the feed is mixed (mixer 10) with finely divided coal and catalyst from line 8 to disperse the coal and catalyst in the heavy oil. Hydrogen is introduced via conduit 62 and constitutes fresh hydrogen via conduit 6, recycled gases via conduit 52 or mixtures thereof. It is an essential feature of this invention that the added coal and catalyst be highly dispersed. The added coal and dispersed catalyst particles are mixed in mixing zone 10 with feed to form a slurry, preferably a dispersion or uniform distribution of particles within the feed, which is introduced into a first-zone thermo-catalytic reactor(s) 20 via conduit 18 together with heavy oil feed and hydrogen-rich gas via conduit 58. Coal is added in the mixture in a concentration relative to the total heavy oil feedstock from 0.5 to 40 percent by weight, preferably 0.5 to 20 percent by weight and more preferably from about 3 to 10 percent by weight. About 3 to 10 percent coal addition will be suitable for most feeds and operations. High volatile bituminous coals are preferred due to their high hydroaromatic content and ease of liquefaction, but coals of other rank may be suitable. The coal particles must be finely divided, having a maximum diameter of about 40 mesh U.S. sieve series, preferably smaller than 100 mesh and more preferably under 10 microns.

[0041] The dispersed catalyst is present in the mixture in a concentration relative to the feedstock of from about 0.1 to 5 percent by weight, preferably 0.5 to 1 percent by weight. Suitable dispersed catalyst particles would be the oxides or sulfides of metals selected from Groups VIb, VIIb and VIIIb. It is preferred that the dispersed catalyst not be supported on a base material. The dispersed catalyst may be either synthetic or naturally occurring minerals such as limonite. The particles should also be finely divided, having a maximum diameter of about 40 mesh U.S. sieve series, and preferably smaller than 100 mesh, and most preferably less than 10 microns. In one embodiment, naturally occurring catalyst are preferred. Such catalysts are effective, relatively cheap and widely available in sufficient quantities. Finely ground limonite, a naturally occurring iron oxide/hydroxide mineral is especially preferred.

[0042] Prior to introduction into the thermo-catalytic zone, the feedstock slurry and hydrogen-containing streams are heated to provide an operating temperature of 400°C to 480°C, preferably 425°C to 470°C, in the zone. This heating may be done to the entire feed to the zone or may be accomplished by segregated heating of the various components or combinations of the components of the total feed (for example, feed-solids slurry, feed-gas mixture, feed only, gas only).

[0043] The heated combined oil, hydrogen-rich gas, coal and catalyst pass by line 15 to an upflow thermo-catalytic slurry reactor(s) 20 and out by conduit 25 to cooling means 30 and by conduit 35 to hydrotreating reactor(s) 40. Hydrogen-rich gas may be added by line 28. In addition to cooling the thermo-catalytic effluent stream, this gas addition will result in higher hydrogen partial pressure and lead to more efficient usage of the hydrotreater catalyst. The short route of products from reactor(s) 20 to reactor 40 helps to minimize asphaltene and mesophase production. After effecting hydrotreatment sufficient to stop the condensation of cracked fragments, it is desirable to remove all or a portion of the gas that is present before further treatment of the heavy products. Since small quantities of water and light gases are produced in the thermo-catalytic zone, the catalyst in the catalytic-hydrotreating zone may be subjected to a slightly lower hydrogen partial pressure than if these materials were absent. Thus the effluent from reactor 40 is passed by line 41 to separator 42. Preferably, the entire bottoms stream from separator 42 is passed by line 43 to the second catalytic-hydrotreating zone 44. Hydrogen–rich gas is added to the separator bottoms stream through conduit 29. Furthermore, this inter-zone removal of the carbon monoxide and other oxygen-containing gases may reduce the hydrogen consumption in the catalytic-

hydrotreating zone. The removal of all or a portion of the gas from the initial catalytic-hydrotreating zone might also be done to provide improved hydrodynamics in the downstream catalytic-hydrotreating zone. In any case, the removal of gas is to be done in a manner that does not cause significant delay in the movement of solids-containing liquids from the initial catalytic-hydrotreating zone 40 to the second catalytic-hydrotreating zone 44 where the process conditions are more favorable for the hydro-treatment of heavy hydrocarbon molecules. The hydrogen-rich stream from the separator (conduit 46) is then cooled and passes into separator 48. The liquid hydrocarbon phase from separator 48 is passed to atmospheric distillation by conduit 49. The gas phase (conduit 51) from separator 48 may be treated and recycled to the thermo-catalytic and/or the catalytic-hydrotreating zone.

[0044] Effluent from reactor 44 passes by conduit 45 to separator 50 where the gas phase is separated from the liquid/solids phase. The gas phase (conduit 53) may be treated and recycled back to the thermo-catalytic and/or the catalytic-hydrotreating zone. The liquid/solids bottoms from the separator 50 passes by conduit 55 to atmospheric distillation column 60 where gases are removed by conduit 66 and liquid fractions are removed as schematically shown by conduit 64. In commercial operation several streams of different boiling range products may be separately removed. The bottoms stream (conduit 65) is further distilled in vacuum column 70 to separate a vacuum distillate product (conduit 72) from a solids-containing vacuum bottoms stream (conduit 75). In some cases it may be desirable to recycle all or a portion of these streams back to the feed system via conduits 76 and/or 78.

[0045] Other reaction conditions in the thermo-catalytic zone include residence time of from 0.5 to 3 hours, preferably 0.5 to 1.5 hours; a hydrogen partial pressure in the range of 35 to 300 atmospheres, preferably 100 to 200 atmospheres, and more preferably 100 to 175 atmospheres; and a hydrogen gas rate of 350 to 3000 liters per liter of feed mixture and preferably 400 to 2000 liters per liter of feed mixture. Under these conditions, a significant amount of the hydrocarbons in the feedstock that boils above 540°C. is converted to hydrocarbons boiling below 540°C. In this invention, the percentage of hydrocarbons that boils above 540°C. that is converted to hydrocarbons boiling below 540°C is at least 50 percent, more preferably 75 percent and most preferably more than 90 percent.

[0046] The reactor(s) in both parts of the catalytic-hydrotreating reaction zone may be fixed, ebullating, or moving bed all of which are well known to those skilled in the art.

[0047] In the catalytic-hydrotreating reaction zones, hydrogenation is the predominant reaction. It further stabilizes unstable molecules from the thermo-catalytic zone and also removes heteroatoms such that the product will also have been substantially desulfurized, denitrified, and deoxygenated. Some cracking also occurs in the catalytic-hydrotreating zone such that some higher-molecular-weight compounds are converted to lower-molecular-weight compounds.

[0048] Catalyst used in the catalytic-hydrotreating zone may be any of the well-known, commercially available hydroprocessing catalysts. A suitable catalyst for use in this reaction zone comprises a hydrogenation component supported on a suitable refractory base. Suitable bases include silica, alumina, or a composite of two or more refractory oxides. Suitable hydrogenation components are selected from Group VIb, VIIb, and metals, VIIIb Group metals and their oxides, sulfides or mixture thereof. Particularly useful are cobalt-molydenum, nickel-molybdenum, or nickel-tungsten.

[0049] In the catalytic-hydrotreating sub-zones, it is preferred to maintain the temperature below 425C, with a typical operating range of preferably 340°C to 425C, and more preferably 360°C to 415C. to prevent catalyst fouling. Other hydrocatalytic conditions include a hydrogen partial pressure from 35 atmospheres to 300 atmospheres, preferably 100 to 200 atmospheres, and more preferably 100 to 175 atmospheres; a hydrogen flow rate of 300 to 1500 liters per liter of feed mixture, preferably 350 to 1000 liters per liter of feed mixture; and a residence times in the range of 0.3 to 4 hours, preferably 0.5 to 3 hours with typically 10-20% of this total time in the first catalytic-hydrotreating zone and the remaining time in the second catalytic-hydrotreating zone.

[0050] Typical heavy hydrocarbonaceous feedstocks of the kind that find application in the process of this invention often contain undesirable amounts of metallic contaminants. Unless removed, these contaminants can result in deactivation of the second-zone hydrotreating catalyst, and/or plugging of the catalyst bed resulting in an increase in the pressure drop in the bed of supported hydrotreating catalyst. The present invention is well suited for the processing of feeds that are high in metallic contaminants because most of these contaminants are removed from the feed and deposited on un-dissolved coal and ash. If a relatively low amount of coal is used or if the coal is insufficient in un-dissolved coal and/or ash, additional coal ash may be added to aid in metals removal. The present invention is also particularly well suited for feeds that are derived from crudes that are high in residuum content, especially those that are also high in contaminants, since high quality products can be obtained from these lower cost crudes.

[0051] The process of the present invention produces liquid products, a significant portion of which boils below 540°C and which is suitable for processing to transportation fuels. The normally liquid products, that is, all of the product fractions boiling above C4, have a specific gravity in the range of naturally occurring petroleum stocks. Additionally, relative to the feed, the total product will have at least 80 percent of sulfur removed and at least 30 percent of nitrogen removed. Products boiling in the transportation fuel range may require additional upgrading prior to use as transportation fuels.

[0052] The process is operated at conditions and with sufficient severity to convert at least fifty (50) percent of the heavy oil feedstock boiling above 540°C to products boiling below 540°C, and preferably at least seventy-five (75) percent and more preferably at least ninety (90) percent.

[0053] In this specification and drawing, the invention has been described with reference to specific embodiments. It will, however, be evident that various modifications and changes can be made thereto without departing from the broader spirit and scope of the invention as set forth in the appended claims. The specification is, accordingly, to be regarded in an illustrative rather than a restrictive sense. Therefore, the scope of the invention should be limited only by the appended claims.

CLAIMS

1. A process for conversion of heavy oils to produce lower boiling hydrocarbon products comprising; dispersing finely divided coal and catalyst in a heavy oil feedstock, heating and passing the dispersed mixture together with hydrogen to a first reaction zone, the product of which is reduced in temperature and passed to a second reaction zone having a supported hydrotreating catalyst and wherein the first and second reaction zones are close-coupled, operated at elevated temperature and pressure, the first reaction zone is a thermo-catalytic reactor(s) and the second reaction zone is comprised of at least two catalytic-hydrotreating reactors in series with a hot separator between reactors that removes light products and gases and passes its liquid/solid phase to the downstream catalytic-hydrotreating reactors; and recovering the product of the catalytic-hydrotreating zone.

2. The process of claim 1 wherein substantially all effluent from the thermo-catalytic zone is passed into the catalytic-hydrotreating zone.

3. The process of claim 1 wherein the dispersed catalysts and supported catalysts are the oxides or sulfides of metals chosen from the Groups VIb, VIIb and VIIIb metals.

4. The process of claim 1 wherein the dispersed catalysts are either a synthetic catalyst or a naturally occurring material.

5. The process of claim 5 wherein the dispersed catalyst is limonite, a naturally occurring iron oxide/hydroxide mineral.

6. The process of claim 1 wherein the temperature of said thermo-catalytic zone is maintained within a range of 400 to 480°C.

7. The process of claim 1 wherein the temperature of said thermo-catalytic zone is maintained within a range of 425°C to 470°C.

8. The process of claim 1 wherein the products from the catalytic-hydrotreating reactor(s) are separated into gaseous, liquid and a liquid/solid bottom fractions and wherein a portion of the liquid and/or liquid/solid fraction bottoms is recycled back to the feed system.

9. The process of claim 1 wherein the products from the catalytic-hydrotreating zone are separated into gaseous and liquid/solid bottom fractions and wherein a portion of a gaseous fraction containing hydrogen is recycled to the hydrotreating reaction zone.

10. The process of claim 1 wherein the products from the catalytic-hydrotreating zone are separated into gaseous, liquid, and liquid/solid bottom fractions and wherein a portion of a gaseous fraction containing hydrogen is recycled to thermo-catalytic reaction zone and/or the reactors in the catalytic-hydrotreating zone.

11. The process as claimed in claim 1 wherein the temperature of the catalytic-hydrotreating zone is 340°C to 425°C.

12. The process as claimed in claim 1 wherein the temperature of the catalytic-hydrotreating zone is preferably360°C to 415°C.

13. The process as claimed in claim 1 wherein the amount of heavy oil in the feedstock is converted to hydrocarbons boiling below 540°C is at least 50 percent.

14. The process as claimed in claim 1 wherein the amount of heavy oil in the feedstock is converted to hydrocarbons boiling below 540°C is preferably at least 90 percent.

15. The process of claim 1 wherein said heavy oil feedstock is selected from the group consisting of crude petroleum, topped crude petroleum, reduced crudes, petroleum residua from atmospheric or vacuum distillations, solvent deasphalted tars and oils, heavy hydrocarbonaceous liquids derived from coal, bitumen, or coal tar pitches.

16. The process of claim 1 wherein said heavy oil feedstock is co-processed with oils such as VGO, Coker Gas Oil, and/or FCC Cycle Oil.

17. The process of claim 1 wherein the concentration of coal dispersed in the total liquid hydrocarbon feed to the thermo-catalytic zone is between 0.5 and 40 percent by weight.

18. The process of claim 1 wherein the concentration of coal dispersed in the total liquid hydrocarbon feed to the thermo-catalytic zone is between 0.5 to 20 percent by weight.

19. The process of claim 1 wherein the concentration of coal dispersed in the total liquid hydrocarbon feed to the thermo-catalytic zone is about 3 to 10 percent by weight.

20. The process of claim 1 wherein the amount of dispersed catalyst in the feed to the thermocatalytic zone is from about 0.1 to 5 percent by weight.

21. The process of claim 1 wherein the residence time of the material in the thermo-catalytic reaction zone is from about 0.5 to 3 hours.

22. The process of claim 1 wherein the total residence time of material in the catalytic-hydrotreating zone is from about 0.3 to 4 hours and the residence time in the zone that is upstream of the hot separator is 0.1 to 1 hour.

23. The process of claim 1 wherein the supported catalyst in said catalytic-hydrotreating zone is maintained in a fixed, ebullated or moving bed(s) within the reaction zone.

24. The process of claim 1 wherein the process is maintained at a hydrogen partial pressure from about 35 atmospheres to 300 atmospheres.

25. The process as claimed in claim 1 wherein said metal contaminants in the feedstock include nickel, vanadium, and iron and where they are substantially removed from the feedstock in the thermo-catalytic zone.

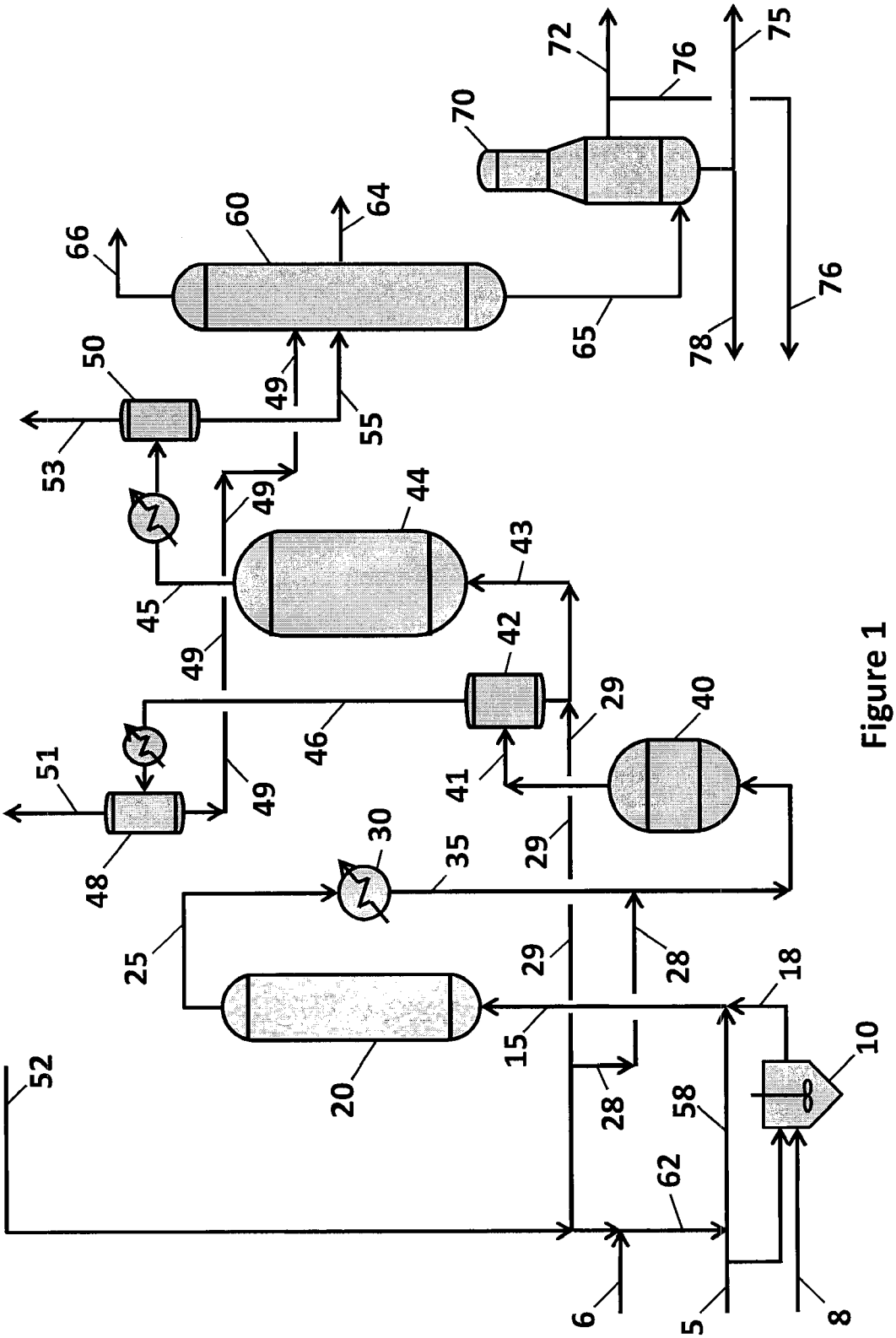

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Figure 1