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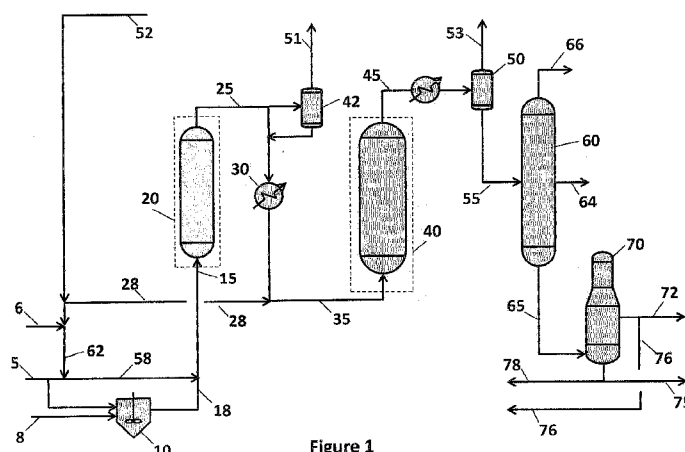


Figure 1

(57) Abstract: A process for hydroconversion of heavy oil feedstocks that effectively controls the condensation of asphaltenes by utilizing a two-zone, close-coupled reactor(s) combination comprising an ebullating bed thermo-catalytic zone operated at high temperature to achieve high conversion of the heavy oil to lower boiling point products, followed by a closely-coupled, catalytic-hydro-treating second zone which may comprise fixed, moving and/or ebullated reactors wherein the first zone liquid effluent is stabilized and reduced in heteroatom content. This close-coupled combination converts heavy hydrocarbonaceous feedstocks, a significant portion of which boils above 540°C, to high yields of high quality products boiling below 540°C. In cases with heavy oil feedstocks that are more difficult to process, a dispersed catalyst and/or dispersed coal may be added to the first zone feed to further promote the conversion to lower boiling point products.

TWO-ZONE, CLOSE-COUPLED, HEAVY OIL HYDROCONVERSION PROCESS UTILIZING AN EBULLATING BED FIRST ZONE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims benefit of Provisional application No. 61/601,366, filed 21 February 2012.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] 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 for converting petroleum heavy oils that provides improved effectiveness for high conversion and control of condensation reactions to produce stable high-quality products.

Background

[0003] 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 boiling at elevated temperatures, particularly those temperatures above 540°C. High conversions to stable, quality products are desirable in order to avoid producing significant quantities of low 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 by-product.

[0004] Higher liquid conversions can be achieved with conventional ebullated bed technologies. However, technologies based on the use of ebullating beds, even those with enhancements such as the use of multiple stages in series or the addition of organometallic dispersed catalysts suffer limitations due to the instability of the fuel oil product and refractive nature of the products – making further upgrading difficult, and their limited ability to deal with high-metals-containing feeds. Current approaches are now focusing 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.

[0005] Severe conditions are required in order to achieve high conversions which, while producing desirable lighter fractions, can also produce thermally cracked fragments and asphaltenes that form mesophase masses. Unless controlled, the cracked fragments undergo condensation reactions to 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. Therefore, the key to high conversion and product quality is the management of the asphaltenes which are produced at severe operating conditions.

[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. Pat. No. 6,270,654 Colyar, et al.; U.S. Pat. No. 7,449,103, Lott, et al.; U.S. Pat. No. 7,815,870, Lott et al. U.S. Patent No. 4,851,107, Kretschmar, et al., U.S. Pat. App. No. 2008/0156693 A1, Okui, et al., US Patent No. 3,70,5092, Gatsis., U.S. Pat. App No. 13/116,195, Lap-Keung Lee, et al., U.S. Patent No. 6,660,157, Que Guohe et al., U. S. Patent No. 7,708,877, Darush Farshid, et al.

[0007] In a broad sense the present invention relates to a process for conversion of heavy oils to produce lower boiling hydrocarbon products comprising; heating the heavy oil feedstock and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is an ebullating bed reactor(s) operating at thermo-catalytic conditions and the second reaction zone is a fixed, moving, or ebullated bed reactor(s) operating at catalytic-hydrotreating conditions; and recovering the product of the second reaction zone. The use of an ebullating bed has the effect of providing the conditions for an active thermo-catalytic reaction, while keeping the catalyst in the reactor, such that a more expensive catalyst may be used without raising the cost of operation.

[0008] In a further embodiment the process for conversion of heavy oils to produce lower boiling hydrocarbon products comprises; dispersing finely divided coal in a heavy oil feedstock, heating and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is an ebullated bed reactor(s) operating at thermo-catalytic conditions and the second reaction zone is fixed, moving or ebullating bed reactor(s) operating at catalytic-hydrotreating conditions; and recovering the product of the second reaction zone, with the associated benefit of coal being an effective hydrogen donor in the process and the coal ashes providing effective metal scavenging.

[0009] In a further embodiment the process for conversion of heavy oils to produce lower boiling hydrocarbon products comprises; dispersing a finely divided catalyst in a heavy oil feedstock, heating and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is an ebullated bed reactor(s) operating at thermo-catalytic conditions and the second reaction zone is fixed, moving or ebullating bed reactor(s) operating at catalytic-hydrotreating conditions; and recovering the product of the second reaction zone, with the associated benefit of the dispersed catalyst being synergetically active in the thermo-catalytic reaction.

[0010] In a further embodiment a finely divided dispersed catalyst passes together with the heavy oil feedstock and finely divided coal into the first reaction zone.

[0011] In a further embodiment substantially all effluent from the first reaction zone is passed into the second reaction zone.

[0012] In a further embodiment some gaseous product is removed from the product of the first reaction zone before passing to the second reaction zone .

[0013] In a further embodiment the catalyst of the first zone comprise an oxide or a sulfide of metals chosen from the Groups VIb, VIIb and VIIIb metals.

[0014] In a further embodiment the dispersed catalysts of the first zone are either a synthetic catalyst or a naturally occurring material.

[0015] In a further embodiment the dispersed catalyst is limonite, a naturally occurring iron oxide/hydroxide mineral.

[0016] In a further embodiment the temperature of said first zone ebullating bed reactor(s) is maintained within a range of between 400°C to 480°C.

[0017] In a further embodiment the temperature of said first zone ebullating bed reactor(s) is maintained within a range of between 425°C to 489°C.

[0018] In a further embodiment the products from the second zone catalytic-hydrotreating reactor(s) are separated into gaseous and liquid fractions and wherein a portion of the liquid is recycled back to the feed system.

[0019] In a further embodiment the products from the second zone catalytic-hydrotreating reactor(s) are separated into gaseous, liquid and a liquid/solid bottom fractions and wherein a portion of the liquid and/or the liquid/solid bottoms fraction is recycled back to the feed system.

[0020] In a further embodiment the effluent from the catalytic-hydrotreating second zone are separated into gaseous and non-gaseous fractions and wherein a portion of the gaseous fraction containing hydrogen is recycled to the ebullating bed first zone.

[0021] In a further embodiment the effluent from the catalytic-hydrotreating second zone are separated into gaseous and non-gaseous fractions and wherein a portion of the gaseous fraction containing hydrogen is recycled to the second zone.

[0022] In a further embodiment the temperature of the catalytic-hydrotreating second zone is between 340°C to 425°C.

[0023] In a further embodiment the amount of heavy oil in the feedstock which is converted to hydrocarbons boiling below 540°C is at least 50 percent.

[0024] In a further embodiment the amount of heavy oil in the feedstock which is converted to hydrocarbons boiling below 540°C is preferably at least 90 percent.

[0025] 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 heavy hydrocarbonaceous liquids derived from coal, bitumen, or coal tar pitches.

[0026] In a further embodiment said heavy oil feedstock is co-processed with oils such as VGO, Coker Gas Oil, Solvent Deasphalted Oil and FCC Cycle Oil.

[0027] In a further embodiment the concentration of coal dispersed in the feed to the ebullating bed first zone is less than 40 percent by weight.

[0028] In a further embodiment the concentration of coal dispersed in the feed to the ebullating bed first zone is less than 20 percent by weight.

[0029] In a further embodiment the concentration of coal dispersed in the feed to the ebullating bed first zone is less than 10 percent by weight.

[0030] In a further embodiment the amount of dispersed catalyst in the feed to the ebullated bed first zone is less than 5 percent by weight.

[0031] In a further embodiment the residence time of the material in the ebullating bed first zone is from about 0.5 to 3 hours.

[0032] In a further embodiment the residence time of material in the catalytic-hydrotreating second reaction zone is from about 0.3 to 4 hours.

[0033] In a further embodiment the supported catalyst in said second zone is maintained in a fixed, ebullated or moving bed(s) within the reaction zone.

[0034] In a further embodiment the process is maintained at a hydrogen partial pressure from about 35 atmospheres to 300 atmospheres.

[0035] In a further embodiment metal contaminants in the feedstock include nickel, vanadium, and iron and are substantially removed from the feedstock in the first thermo-catalytic zone.

SUMMARY

[0036] In a broad form, the present invention relates to a process for conversion of heavy oils to produce lower boiling hydrocarbon products comprising; heating the heavy oil feedstock and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure (thermo-catalytic conditions), the product of which is reduced in temperature (to catalytic hydrotreating conditions) while maintaining pressure and passed to a second reaction zone having a supported hydrotreating catalyst and wherein the first reaction zone is an ebullating bed reactor(s) and the second reaction zone is a catalytic-hydrotreating reactor(s) which may be fixed bed, moving bed and/or ebullating bed in type; and recovering the product of the second reaction zone. The use of an ebullating bed has the benefit that the catalyst remains in the reactor, such that a more expensive catalyst may be used as it will remain in the process for a much longer time than a dispersed catalyst, unless the dispersed catalyst is recycled to the process.

[0037] In a further embodiment the process comprises the step of dispersing finely divided coal in a heavy oil feedstock, heating and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is an ebullating bed reactor(s) and the second reaction zone is a catalytic-hydrotreating reactor(s) which may be fixed

bed, moving bed and/or ebullating bed in type; and recovering the product of the second reaction zone. The use of finely divided coal has the following benefits: (1) coal oil derived from coal is an effective hydrogen donor which helps to stabilize the free radical fragments and thus reduce formation of asphaltenes (2) the coal oil acts as a solubilizer for asphaltenic molecules which inhibits their agglomeration and (3) the coal and coal ash sequester metals contained in the heavy oil.

[0038] In a further embodiment this process comprises the step of dispersing a finely divided, catalyst in a heavy oil feedstock, heating and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is an ebullating bed reactor(s) and the second reaction zone is a catalytic-hydrotreating reactor(s) which may be fixed bed, moving bed and/or ebullating bed in type; and recovering the product of the second reaction zone. The benefit of adding a finely divided catalyst is that activity of the supported catalyst may be combined with an activity of the same or different reaction mechanism.

[0039] In a further embodiment a finely divided dispersed catalyst passes together with the heavy oil feedstock and finely divided coal into the first reaction zone. This has the effect of added finely divided catalyst and finely divided coal in a single process step.

[0040] In a further embodiment substantially all effluent from the first reaction zone is passed into the second reaction zone. This has the effect of reducing the risk of removing the close-coupled nature of the process.

[0041] In a further embodiment some gaseous product is removed from the product of the first reaction zone before passing to the second reaction zone. This has the effect of reducing the process stream to the second reaction zone and thus reducing the reactor volume in the zone.

[0042] In a further embodiment both the dispersed and supported catalysts are the oxides or sulfides of metals chosen from the Groups VIb, VIIb and VIIIb metals. This has the effect of said metals being active in the thermo-catalytic hydrogenation zone.

[0043] In a further embodiment the dispersed catalysts are either a synthetic catalyst or a naturally occurring material, with the associated benefits of synthetic catalysts having well defined activities, but alternatively naturally occurring materials being cost effective.

[0044] In a further embodiment the dispersed catalyst is a naturally occurring iron oxide/hydroxide mineral such as limonite, with the associated benefit of limonite and other iron oxides or iron hydroxides being inexpensive but still catalytically active.

[0045] 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 molecules and are more readily processed to finished fuels.

[0046] The process, in one embodiment, comprises introducing heavy oil feedstock into a first- reaction zone (first zone), comprising an ebullating bed reactor (or reactors in series) in the presence of hydrogen, a supported catalyst and operated at elevated temperature and pressure (thermo-catalytic conditions). As is typical of ebullating bed reactors, the reactor recirculates hydrocarbon from the top to the bottom of the reactor such that the supported catalyst is present as an expanded or ebullated bed. The feedstock is introduced into this first- zone under conditions sufficient to convert a significant amount of hydrocarbons in the feedstock boiling above 540°C to hydrocarbons boiling below 540°C. With feeds that are more difficult to process (those more deficient in hydrogen content or higher in metals content), a dispersed catalyst and /or dispersed coal may be added to the first zone feed to increase conversion, to improve hydrogenation of the feed and to help accommodate the metals that are in the feed. Whether or not a dispersed catalyst and/or coal is added, substantially all of the first zone effluent is passed directly, in a close-coupled manner, into a catalytic-hydrotreating zone (second zone). Inter-zone cooling is provided to reduce the process temperature in the second zone to levels typically used for heavy oil hydrotreating. In the second zone, the first zone effluent is contacted with hydrotreating catalysts under typical hydrotreating conditions. Following the second zone the effluent is recovered .

[0047] In another embodiment of according to the present disclosure a portion of the gaseous products from the first zone is removed. In this embodiment, after a portion of the first zone gaseous products have been removed, substantially all of the first-zone liquid (containing dispersed catalyst and/or dispersed coal if they are used) is passed directly, in a close-coupled manner, into the second zone with inter-zone cooling to reduce temperature prior to the second zone. The first zone liquid effluent (including dispersed solids in cases where a dispersed catalyst or coal have been added to the first zone feed) is contacted in the second zone with hydrotreating catalysts under hydrotreating conditions, and the effluent from catalytic-hydrotreating reaction zone is recovered.

DESCRIPTION OF THE DRAWINGS

[0048] Figure 1 is a schematic flow diagram of a process according to the present disclosure. Both embodiments (with and without any gas removal between the reaction zones) are covered by this single diagram.

DETAILED DESCRIPTION

[0049] The present disclosure relates to a process for hydroconversion of heavy oil feedstocks that effectively controls the condensation of asphaltenes by utilizing a two-zone, close-coupled reactor(s) combination comprising an ebullating bed thermo-catalytic zone operated at high temperature to achieve high conversion of the heavy oil to lower boiling point products followed by a closely-coupled, catalytic-hydrotreating second zone which may comprise fixed, moving and/or ebullated reactors wherein the first zone liquid effluent is stabilized and reduced in heteroatom content. This close-coupled combination 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. In cases with heavy oil feedstocks that are more difficult to process, a dispersed catalyst and/or dispersed coal may be added to the first zone feed to further promote the conversion to lower boiling point products.

[0050] The process, in one embodiment, is a two zone, close-coupled process, the first zone of which encompasses an ebullating-bed, higher-temperature thermo-catalytic zone, wherein the feedstock is substantially converted to lower boiling products. The product of the first zone is cooled somewhat and passed directly, without substantial loss of hydrogen partial pressure, into a second zone, where the first zone effluent is hydrotreated to produce hydrotreated products suitable for further treatment into transportation fuels and other products.

[0051] In the first zone, the ebullating bed catalyst cracks the feedstock. The ebullating bed catalyst also serves to catalyze the hydrogenation of thermally cracked fragments and stabilizes them, thus preventing condensation reactions. For more difficult feeds, a dispersed catalyst may also be introduced to the first zone to increase the cracking and hydrogenation of thermally cracked fragments. In most applications, it will also be advantageous to introduce dispersed coal to the first zone. Conditions in the ebullating bed will convert most of the coal into coal liquids. The ebullating bed catalyst and, if utilized, the dispersed catalyst will hydrogenate the coal liquids, which coal liquids will enhance the hydrogenation of thermally cracked fragments of the heavy oil feed by donating hydrogen to them. The coal liquids also act to solubilize asphaltenes and asphaltene precursors and inhibit the formation of mesophase masses. Also, if coal is introduced, unconverted coal and coal ash will serve to sequester some of the metals that are present in the feedstock. This will result in a reduction of metals fouling of

the first zone supported ebullating bed catalyst and the downstream hydrotreating catalyst in the second zone.

[0052] Even with the presence of catalysts, the high temperature processing in the thermo-catalytic first zone tends to produce unstable products. Because of this fact, the close-coupled lower-temperature second zone plays a key role in the overall process by promptly stabilizing remaining thermally cracked fragments from the first zone. The second zone also serves by hydrogenating products, removing heteroatoms, and effecting some further molecular weight reduction. If cracked fragments from the first zone are not promptly stabilized, it can lead to both the fouling of downstream equipment and the production of poor quality products. Placing the lower-temperature second zone directly after the higher temperature first zone (in a single high pressure loop) assures the prompt saturation of unstable molecules that were created in the first zone. The close-coupling to a lower temperature hydrotreating second zone of the first zone effluent is in contrast to other disclosed technology which does not significantly reduce the operating temperature between sequenced reactors or other technologies which place separations steps directly after a high temperature conversion reactor and do not directly pass the higher molecular weight liquids (or higher molecular weight liquids/solids) into a lower temperature second catalytic-hydrotreating zone for stabilization. The prompt stabilization obtained with the current invention significantly reduces the polymerization of unstable molecules to form undesirable asphaltenes. Thus, the two reaction zones are "close-coupled". Close-coupled then, refers to the connective relationship between these zones. The pressure between the higher temperature conversion thermo-catalytic zone and the lower temperature 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 first zone thermo-catalytic effluent passes from one zone to the other, and there is no more cooling and reheating than necessary. However, it is preferred 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 first zone is cooled to a temperature between 340-425 °C and more preferably 360-415 °C in order to reach a temperature suitable for hydrotreating without excessive fouling of the hydrotreating catalyst in the second catalytic-hydrotreating zone. Some cooling may also be effected by the addition of a fresh, cold, hydrogen-rich stream.

[0053] 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 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, solvent deasphalted oil, and FCC cycle oils may also be favorably co-processed with these heavy oils.

[0054] A second embodiment according to the present disclosure is similar to the first in that it is a two-zone, close-coupled process, the first zone of which encompasses an ebullating-bed, higher-temperature thermo-catalytic zone, wherein the feedstock is substantially converted to lower boiling products followed by a close-coupled, lower-temperature catalytic-hydrotreating zone in which the first zone products are stabilized and treated. However, in some embodiments, it may be desirable to remove a portion of the gas that is present in the first zone effluent stream. Since small quantities of water and light gases are produced in the first zone, the catalyst in the second zone may be subjected to a slightly lower hydrogen partial pressure than if these materials were absent. Thus, in a second embodiment according to the present disclosure the first zone effluent passes to a separator with, preferably, the entire bottoms stream from the separator being passed to the catalytic-hydrotreating second zone. Removal of some or all of the gas phase of the first zone effluent may be done for any of a number of reasons. If hydrogen-rich gas is added to the liquid phase from the separator, the hydrogen partial pressure in the second zone will be increased, thereby improving performance in the second zone. Removal of carbon monoxide and other oxygen-containing gases from the first zone effluent may reduce the associated hydrogen consumption in the second zone. The removal of all or a portion of the gas from the thermo-catalytic first zone might also be done to provide improved hydrodynamics in the downstream second 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 the liquid (or liquid/solids) first zone effluent to the catalytic-hydrotreating second zone where the process conditions are more favorable for the stabilization of heavy hydrocarbon molecules.

[0055] The process according to the present disclosure may be more fully understood by reference to the diagram on Figure 1 which illustrates two embodiments according to the present disclosure. Heavy oil feedstock (hydrocarbonaceous feed-stocks, a significant portion of which boils above 540°C) enters the process by line 5. When it is advantageous to add dispersed catalyst and/or coal to the first zone ebullating bed reactor(s), some portion of the feed is mixed (mixer 10) with finely divided catalyst and/or coal from line 8 to create a dispersion in oil feed.

[0056] When used, the dispersed catalyst is present in the mixture in a concentration relative to the feedstock of from about 0 to 5 percent by weight, preferably 0.2 to 1 percent by weight. Suitable dispersed catalyst particles would be the oxides or sulfides of metals selected from Groups VIb, VIIb and VIIIb. 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.

[0057] When used, coal is added in the mixture in a concentration relative to the feedstock from 0 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.

[0058] Any dispersed catalyst or coal that is to be added is mixed with feed in mixing zone 10 to form a slurry, preferably a dispersion or uniform distribution of particles within feed. Feed from line 5 together with any slurry through line 18 and hydrogen from line 62 all come together in line 15 for introduction into the first zone ebullating bed reactor(s), 20. The hydrogen introduced via line 62 constitutes fresh hydrogen via line 6, recycled gases via line 52 or mixtures thereof. Prior to introduction into the first zone, the feedstock, slurry (if one is utilized), and hydrogen-containing streams are heated to provide an operating temperature of between 400°C to 480°C, preferably 425°C to 470°C, in the first 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). In practice, the streams flowing to the first zone can be introduced as a single stream, 15, as shown in Figure 1 or in segregated fashion.

[0059] After reacting in the ebullating bed reactor(s), 20, of the first zone, the reaction mixture exits by line 25 to cooling means 30 and by line 35 to hydrotreating reactor(s) 40. Hydrogen-rich gas may be added by line 28. In addition to cooling the first zone 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 zone 20 to zone 40 helps to minimize asphaltene and

mesophase production. However, in some embodiments, it may be desirable to remove a portion of the gas that is present in the effluent of the first zone. Since small quantities of water and light gases are produced in the first zone, the catalyst in the second zone may be subjected to a slightly lower hydrogen partial pressure than if these materials were absent. Thus, in some embodiments, effluent from the first zone, 20, passes by line 25 to separator 42. Preferably, the entire bottoms stream from separator 42 is passed to the second zone. Furthermore, this inter-zone removal of the carbon monoxide and other oxygen-containing gases may reduce the hydrogen consumption in the second zone. The removal of all or a portion of the gas from the first zone might also be done to provide improved hydrodynamics in the downstream second 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 first zone to the second zone where the process conditions are more favorable for the stabilization of heavy hydrocarbon molecules. This hydrogen-rich stream (line 51) may be treated and recycled to either zone.

[0060] Effluent from reactor(s) 40 passes by line 45 to separator 50 where the gas phase is separated from the liquid/solids phase. The gas phase (line 53) may be treated and recycled back to the thermocatalytic first zone and/or the catalytic-hydrotreating second zone. The liquid/solids bottoms from the separator 50 passes by line 55 to an atmospheric distillation column 60 where gases are removed by line 66 and liquid fractions are removed as schematically shown by line 64. In operation several streams of different boiling range products may be separately removed. The bottoms stream (line 65) is further distilled in vacuum column 70 to separate a vacuum distillate product (line 72) from a vacuum bottoms stream which will be solids-containing if dispersed catalyst and/or coal has been added to the hydrocarbon feed(line 75). In some cases it may be desirable to recycle all or a portion of these streams back to the feed system via lines 76 and/or 78.

[0061] Reaction conditions in the ebullating bed first zone are typical in severity as disclosed by others for ebullating bed reactors processing residuum feedstocks. Temperatures range above 430°C; residence times range from 0.5 to 3 hours; and hydrogen partial pressure ranges from 35 to 300 atmospheres, preferably 100 to 200 atmospheres, and more preferably 100 to 175 atmospheres. Under these conditions, a significant amount of the hydrocarbons in the feedstock boiling above 540°C. is converted to hydrocarbons boiling below 540°C. According to the present disclosure, the percentage of hydrocarbons boiling above 540°C. converted to those boiling below 540°C are at least 50 percent, more preferably at least 75 percent and most preferably more than 90 percent.

[0062] When dispersed catalysts and/or coal are not used to enhance to performance in the first zone ebullating bed reactor(s), the supported catalyst will be typical of that disclosed by others for use in

ebullating beds. However, if supplemented with a dispersed catalyst and/or coal, the supported ebullating bed catalyst can be reduced in metals content which should result in a lower cost catalyst. Addition of coal would also reduce the amount of metals that would deposit on the supported catalyst. This would further increase the savings in the cost of supported catalyst.

[0063] The lower-temperature catalytic-hydrotreating second zone, 60, may utilize a reactor (or reactors in series) that is fixed bed, ebullating bed, or moving bed in nature, all of which are well known to those skilled in the art.

[0064] Hydrogenation is the predominant reaction in the second zone. This stabilizes unstable molecules from the first zone and also saturates aromatic molecules. The second zone also removes heteroatoms such that the product will also have been substantially desulfurized, denitrified, and deoxygenated. Some cracking also occurs simultaneously, such that some higher-molecular-weight compounds are converted to lower-molecular-weight compounds.

[0065] Catalyst used in the second 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 metals, Group VIIb, Group VIII metals and their oxides, sulfides or mixture thereof. Particularly useful are cobalt-molybdenum, nickel-molybdenum, or nickel-tungsten.

[0066] In the second zone, it is preferred to maintain the temperature below 425°C, preferably in the range of 340°C to 425°C, and more preferably between 360°C to 415°C. 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 time in the range of 0.3 to 4 hours, preferably 0.5 to 3 hours.

[0067] 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. An embodiment according to the present disclosure that utilizes a lower cost ebullating bed catalyst together with added dispersed coal particles is well suited for the processing of feeds that are high in metallic contaminants. 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.

[0068] A process according to the present disclosure produces liquid products, a significant portion of which boils below 540°C and which are 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 a transportation fuel.

[0069] 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 conversion and more preferably to at least ninety (90) percent conversion.

[0070] 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; heating the heavy oil feedstock and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is an ebullating bed reactor(s) operating at thermo-catalytic conditions and the second reaction zone is a fixed, moving, or ebullated bed reactor(s) operating at catalytic-hydrotreating conditions; and recovering the product of the second reaction zone.
2. A process for conversion of heavy oils to produce lower boiling hydrocarbon products comprising; dispersing finely divided coal in a heavy oil feedstock, heating and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first reaction zone is a fixed, moving, or ebullated bed reactor(s) operating at thermo-catalytic conditions and the second reaction zone is an ebullating bed reactor(s) operating at catalytic-hydrotreating conditions; and recovering the product of the second reaction zone.
3. A process for conversion of heavy oils to produce lower boiling hydrocarbon products comprising; dispersing a finely divided catalyst in a heavy oil feedstock, heating and passing it into a first reaction zone comprising an ebullating bed reactor(s), in the presence of hydrogen and a supported catalyst, and operated at elevated temperature and pressure, 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 and operated at elevated temperature and pressure, and the first

- reaction zone is a fixed, moving, or ebullated bed reactor(s) operating at thermo-catalytic conditions and the second reaction zone is an ebullating bed reactor(s) operating at catalytic-hydrotreating conditions; and recovering the product of the second reaction zone.
4. The process of claim 2 wherein a finely divided dispersed catalyst passes together with the heavy oil feedstock and finely divided coal into the first reaction zone.
 5. The process of claims 1, 2, 3, and 4 wherein substantially all effluent from the first reaction zone is passed into the second reaction zone.
 6. The process of claims 1, 2, 3, and 4 wherein some gaseous product is removed from the product of the first reaction zone before passing to the second reaction zone .
 7. The process of claims 1, 2, 3 and 4 wherein at least one catalyst of the first zone comprise an oxide or a sulfide of metals chosen from the Groups VIb, VIIb and VIIIb metals.
 8. The process of claims 3 and 4 wherein the dispersed catalysts are either a synthetic catalyst or a naturally occurring material.
 9. The process of claim 8 wherein the dispersed catalyst is limonite, a naturally occurring iron oxide/hydroxide mineral.
 10. The process of claims 1, 2, 3, and 4 wherein the temperature of said first zone ebullating bed reactor(s) is maintained within a range of between 400C to 480°C.
 11. The process of claims 1, 2, 3, and 4 wherein the temperature of said first zone ebullating bed reactor(s) is maintained within a range of between 425°C to 470°C.
 12. The process of claim 1 wherein the products from the second zone catalytic-hydrotreating reactor(s) are separated into gaseous and liquid fractions and wherein a portion of the liquid is recycled back to the feed system.
 13. The process of claims 2, 3, and 4 wherein the products from the second zone catalytic-hydrotreating reactor(s) are separated into gaseous, liquid and a liquid/solid bottom fractions and wherein a portion of the liquid and/or the liquid/solid bottoms fraction is recycled back to the feed system.
 14. The process of claims 1, 2, 3, and 4 wherein the effluent from the catalytic-hydrotreating second zone are separated into gaseous and non-gaseous fractions and wherein a portion of the gaseous fraction containing hydrogen is recycled to the ebullating bed first zone.

15. The process of claims 1, 2, 3, and 4 wherein the effluent from the catalytic-hydrotreating second zone are separated into gaseous and non-gaseous fractions and wherein a portion of the gaseous fraction containing hydrogen is recycled to the second zone.
16. The process as claimed in claims 1, 2, 3, and 4 wherein the temperature of the catalytic-hydrotreating second zone is between 340°C to 425°C.
17. The process as claimed in claims 1, 2, 3, and 4 wherein the temperature of the catalytic-hydrotreating second zone is between 360°C to 415°C.
18. The process as claimed in claims 1, 2, 3, and 4 wherein the amount of heavy oil in the feedstock which is converted to hydrocarbons boiling below 540°C is at least 50 percent.
19. The process as claimed in claim 1, 2, 3, and 4 wherein the amount of heavy oil in the feedstock which is converted to hydrocarbons boiling below 540°C is preferably at least 90 percent.
20. The process of claims 1, 2, 3, and 4 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 heavy hydrocarbonaceous liquids derived from coal, bitumen, or coal tar pitches.
21. The process of claims 1, 2, 3, and 4 wherein said heavy oil feedstock is co-processed with oils such as VGO, Coker Gas Oil, Solvent Deasphalted Oil and FCC Cycle Oil.
22. The process of claims 2 and 4 wherein the concentration of coal dispersed in the feed to the ebullating bed first zone is less than 40 percent by weight.
23. The process as claimed in claims 2 and 4 wherein the concentration of coal dispersed in the feed to the ebullating bed first zone is less than 20 percent by weight.
24. The process as claimed in claims 2 and 4 wherein the concentration of coal dispersed in the feed to the ebullating bed first zone is less than 10 percent by weight.
25. The process of claims 3 and 4 wherein the amount of dispersed catalyst in the feed to the ebullated bed first zone is less than 5 percent by weight.
26. The process of claims 1, 2, 3, and 4 wherein the residence time of the material in the ebullating bed first zone is from about 0.5 to 3 hours.

27. The process of claims 1, 2, 3, and 4 wherein the residence time of material in the catalytic-hydrotreating second reaction zone is from about 0.3 to 4 hours.
28. The process as claimed in claims 1, 2, 3, and 4 wherein the supported catalyst in said second zone is maintained in a fixed, ebullated or moving bed(s) within the reaction zone.
29. The process as claimed in claims 1, 2, 3, and 4 wherein the process is maintained at a hydrogen partial pressure from about 35 atmospheres to 300 atmospheres.
30. The process as claimed in claims 1, 2, 3, and 4 wherein metal contaminants in the feedstock include nickel, vanadium, and iron and where they are substantially removed from the feedstock in the first thermo-catalytic zone.

