TARGETED HYDROGENATION HYDROCRACKING

Inventor: Subhasis Bhattacharya, Walnut Creek, CA (US)

Correspondence Address:
CHEVRON CORPORATION
P.O. BOX 6006
SAN RAMON, CA 94583-0806 (US)

Assignee: Chevron U.S.A. Inc.

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ABSTRACT

This invention is directed to a process scheme in which a partial conversion hydrocracking (HCR) unit, preferably preceded by a hydrotreating unit, feeds unconverted oil to a FCC (fluid catalytic cracking) unit. Most refineries run the FCC unit at full capacity for optimal asset utilization. During shutdowns of Residue Desulfurization unit(s) which feed an FCC unit, it is desirable to reduce the conversion in the FCC feed hydrocracker. In this way, the feed to FCC unit is maximized. Jet and Diesel products that conform to specifications may be produced during low conversion HCR operation. Furthermore, undesirable over-saturation of the unconverted oil (UCO) from the HCR unit feeding the FCC unit can be avoided. Excess hydrogen consumption can also be avoided. Normally, further aromatic saturation of the middle distillate products from a low conversion HCR is achieved in a separate, post treatment, unit.
TARGETED HYDROGENATION HYDROCRACKING

FIELD OF THE INVENTION

[0001] This invention is directed to a partial conversion hydrocracking (HCR) unit, in which unconverted oil is fed to a Fluid Catalytic Cracking (FCC) unit.

BACKGROUND OF THE INVENTION

[0002] In the refining of crude oil, vacuum gas oil hydrotreaters and hydrocrackers are employed to remove impurities such as sulfur, nitrogen and metals from the feed. Typically, the middle distillate boiling material (boiling in the range from 250°F - 735°F) from VGO hydrotreating or moderate severity hydrocrackers does not meet the smoke point, the cetane number or the aromatic specification required.

[0003] Removal of these impurities in subsequent hydroprocessing stages (often known as upgrading), creates more valuable middle distillate products. Hydroprocessing technology (which encompasses hydrotreating, hydrocracking and hydrodewaxing processes) aims to increase the value of the crude oil by fundamentally rearranging molecules. The end products are also made more environmentally friendly.

[0004] In most cases, this middle distillate is separately upgraded by a middle distillate hydrocracker or, alternatively, the middle distillate is blended into the general fuel oil pool or used as home heating oil. Recently hydroprocessing schemes have been developed which permit the middle distillate to be hydrotreated in the same high pressure loop as the vacuum gas oil hydrotreating reactor or the moderate severity hydrocracking reactor. The investment cost saving and/or utilities saving are significant since a separate middle distillate hydrotreater is not required.

[0005] There are U.S. patents which are directed to multi-stage hydroprocessing within a single high pressure hydrogen loop. In U.S. Pat. No. 6,797,154, high conversion of heavy gas oils and the production of high quality middle distillate products are possible in a single high-pressure loop with reaction stages operating at different pressure and conversion levels. The flexibility offered is great and the refiner is allowed to avoid decrease in product quality while at the same time minimizing the consumption of hydrogen and reducing capital investment.

[0006] U.S. Pat. No. 6,787,025 also discloses multi-stage hydroprocessing for the production of middle distillates. A major benefit of this invention is the potential for simultaneously upgrading difficult cracked stocks such as Light Cycle Oil, Light Coker Gas Oil and Visbroken Gas Oil or Straight-Run Atmospheric Gas Oils utilizing the high-pressure environment required for mild hydrocracking.

[0007] U.S. Pat. No. 7,238,277 provides very high to total conversion of heavy oils to products in a single high-pressure loop, using multiple reaction stages. The second stage or subsequent stages may be a combination of co-current and counter-current operation. The benefits of this invention include conversion of feed to useful products at reduced operating pressures using lower catalyst volumes. Lower hydrogen consumption also results. A minimal amount of equipment is employed. Utility consumption is also minimized.

[0008] U.S. Publication 20050103682 relates to a multi-stage process for hydrotreating gas oils. Preferably, each stage possesses at least one hydrocracking zone. The second stage and any subsequent stages possess an environment having a low heteroatom content. Light products, such as naphtha, kerosene and diesel, may be recycled from fractionation (along with light products from other sources) to the second stage (or a subsequent stage) in order to produce a larger yield of lighter products, such as gas and naphtha. Pressure in the zone or zones subsequent to the initial zone is from 500 to 1000 psig lower than the pressure in the initial zone, in order to provide cost savings and minimize overcracking.

[0009] Most refineries run the FCC unit at full capacity for optimal asset utilization. During planned and/or unplanned shutdown of Residue Desulfurization unit(s) feeding FCC unit, it is desirable to reduce the conversion in the FCC feed hydrocracker in order to maximize the feed to FCC unit. The patents disclosed above do not address the following issues:


[0011] 2. Avoidance of undesirable over-saturation of the unconverted oil (UCO) from the HCR unit feeding FCC unit and reduce hydrogen consumption. Normally, further aromatic saturation of the middle distillate products from a low conversion HCR is achieved in a separate Post Treatment unit.

SUMMARY OF THE INVENTION

[0012] A new process scheme has been developed to design a partial conversion hydrocracking (HCR) unit, feeding the unconverted oil to a FCC unit. The steps of this invention are summarized as follows:

[0013] A method for hydrotreating a hydrocarbon feedstock, said method employing multiple hydroprocessing zones within a single reaction loop, each zone having one or more catalyst beds, comprising the following steps:

[0014] (a) passing a hydrocarbonaceous feedstock to a first hydrotreating zone containing one or more beds containing hydrotreating catalyst, the hydroprocessing zone being maintained at hydrotreating conditions, wherein the feedstock is contacted with catalyst and hydrogen;

[0015] (b) passing the effluent of step (a) to a second hydroprocessing zone containing hydrogen, hydrocarbonaceous compounds boiling at a temperature below the boiling range of the hydrocarbonaceous feedstock, wherein the liquid stream comprising hydrocarbonaceous compounds boiling approximately in the range of said hydrocarbonaceous feedstock;

[0016] (c) passing the vapor stream of step (b) after cooling and partial condensation, to a high pressure separator, wherein the effluent is separated to produce a liquid stream containing hydrogen, hydrocarbonaceous compounds boiling at a temperature below the boiling range of the hydrocarbonaceous feedstock, and a liquid stream comprising hydrocarbonaceous compounds boiling in the high pressure separator and a liquid stream comprising hydrocarbonaceous compounds boiling in the middle distillate range, is passed to a second hydrocracking zone;

[0017] (d) passing the overhead vapor stream from the high pressure separator of step (c), after cooling and contact with water, said vapor stream comprising hydrogen, ammonia, hydrogen sulfide, light gases and naphtha, to a cold high pressure separator, wherein hydrogen, hydrogen sulfide, and light hydrocarbonaceous gases are removed overhead, ammonia is
removed from the cold high pressure separator as ammonium bisulfide in the sour water stripper, and naptha and middle distillates are passed to fractionation.

0018 (e) passing the liquid stream from the hot high pressure separator of step (b) to a hot low pressure separator, where it is flashed to produce an overhead stream comprising gases and a liquid stream comprising unconverted oil.

0019 (f) passing the liquid stream of step (e) which comprises unconverted oil, to a steam stripper, where lighter material is removed overhead as a vapor stream, and a liquid stream, which comprises stripped unconverted oil, is recovered.

BRIEF DESCRIPTION OF THE FIGURE

0020 The FIGURE illustrates the flow scheme of the current invention.

DETAILED DESCRIPTION OF THE INVENTION

0021 Feedstocks

0022 A wide variety of hydrocarbon feeds may be used in the instant invention. Typical feedstocks include any heavy or synthetic oil fraction or process stream having a boiling point above 392°F (200°C). Such feedstocks include vacuum gas oils (VGO), heavy coker gas oil (HCGO), heavy atmospheric gas oil (AGO), light coker gas oil (LCGO), visbreaker gas oil (VBGO), demetallized oils (DMO), vacuum residua, atmospheric residua, deasphalted oil (DAO), Fischer-Tropsch streams, Light Cycle Oil, Light Cycle Gas Oil and other FCC process streams.

0023 Products

0024 The process of this invention is especially useful in the production of middle distillate fractions boiling in the range of about 250-700°F (121-371°C). A middle distillate fraction is defined as having an approximate boiling range from about 250 to 700°F at least 75 vol. %, preferably 85 vol. % of the components of the middle distillate have a normal boiling point of greater than 250°F. At least about 75 vol. %, preferably 85 vol. % of the components of the middle distillate have a normal boiling point of less than 700°F. The term "middle distillate" includes the diesel, jet fuel and kerosene boiling range fractions. The kerosene or jet fuel boiling point range refers to the range between 280 and 525°F (138-274°C). The term "diesel boiling range" refers to hydrocarbons boiling in the range from 250 to 700°F (121-371°C).

0025 Gasoline or naphtha may also be produced in the process of this invention. Gasoline or naphtha normally boils in the range below 400°F (204°C), or C5 to C9 (400°F). Boiling ranges of various product fractions recovered in any particular refinery will vary with such factors as the characteristics of the crude oil source, local refinery markets and product prices.

0026 Conditions

0027 "Hydroprocessing conditions" is a general term which refers primarily to this application to hydrocracking or hydrodetrating.

0028 Hydrodetrating conditions include a reaction temperature between 400°F - 950°F (204°C - 482°C), preferably 600°F - 850°F (315°C - 446°C), a pressure between 500 to 5000 psig (pounds per square inch gauge) (3.5-34.6 MPa), preferably 1000 to 3000 psig (7.0-20.8 MPa); a feed rate (LHSV) of 0.3 hr-1 to 20 hr-1 (v/v) preferably from 0.5 to 4.0; and overall hydrogen consumption 300 to 2000 SCF per barrel of liquid hydrocarbon feed (63.4-356 m3/m3 feed).

0029 Typical hydrocracking conditions include a reaction temperature of from 400°F - 950°F (204°C - 482°C), preferably 600°F - 850°F (315°C - 446°C). Reaction pressure ranges from 500 to 5000 psig (3.5-4.5 MPa), preferably 1000-3000 psig (7.0-20.8 MPa). LHSV ranges from 0.1 to 15 hr-1 (v/v), preferably 0.5 to 5.0 hr-1. Hydrogen consumption ranges from 500 to 2500 SCF per barrel of liquid hydrocarbon feed (89.1-445 m3/m3 feed).

0030 Catalyst

0031 A hydroprocessing zone may contain only one catalyst, or several catalysts in combination.

0032 The hydroprocessing catalyst generally comprises a cracking component, a hydrogenation component, and a binder. Such catalysts are well known in the art. The cracking component may include an amorphous silica/alumina phase and/or a zeolite, such as a Y-type or USY zeolite. Catalysts having high cracking activity often employ REX, REY and USY zeolites. The binder is generally silica or alumina. The hydrogenation component will be a Group VI, Group VII, or Group VIII metal or oxides or sulfides thereof, preferably one or more of molybdenum, tungsten, cobalt, or nickel, or the sulfides or oxides thereof. If present in the catalyst, these hydrogenation components generally make up from about 5% to about 40% by weight of the catalyst. Alternatively, platinum group metals, especially platinum and/or palladium, may be present as the hydrogenation component, either alone or in combination with the base metal hydrogenation components molybdenum, tungsten, cobalt, or nickel. If present, the platinum group metals will generally make up from about 0.1% to about 2% by weight of the catalyst.

0033 Hydrodetrating catalyst is typically a composite of a Group VI metal or compound thereof, and a Group VIII metal or compound thereof supported on a porous refractory base such as alumina. Examples of hydrodetrating catalysts are alumina supported cobalt-molybdenum, nickel sulfide, nickel-tungsten, cobalt-tungsten and nickel-molybdenum.

0034 In some cases, high activity hydrodetrating catalyst suitable for high levels of hydrogenation, is employed. Such catalysts have high surface areas (greater than 140 m2/gm) and high densities (0.7-0.95 gm/cc). The high surface area increases reaction rates due to generally increased dispersion of the active components. Higher density catalysts allow one to load a larger amount of active metals and promoter per reactor volume, a factor which is commercially important. Since deposits of coke are thought to cause the majority of the catalyst deactivation, the catalyst pore volume should be maintained at a modest level (0.4-0.6). A high activity catalyst is at times desired in order to reduce the required operating temperatures. High temperatures lead to increased coking.

Description of the Preferred Embodiment

0035 Please refer to the FIGURE:

0036 In this process scheme, fresh feed (Stream 9) is passed to the top of fixed bed hydrodetrater reactor 10. Hydrogen passes through stream 1. Stream 29 is a sidestream from stream 1. From stream 29, streams 3 and 4 add hydrogen in between the first and second beds, and second and third beds of reactor 10 respectively. Hydrodetrater 10 is loaded with a high activity hydrodetrating catalyst, where most of the feed...
impurities (heteroatoms) such as nitrogen, sulfur, etc. are removed and some degree of aromatic saturation is achieved.

[0037] The hydrotreated reactor effluent (stream 12) exchanges heat in exchanger 5 with the reactor feed (stream 2 prior to entering the exchanger 5 and stream 9 upon leaving the exchanger 5). Stream 12 is flashed in high pressure separator 40 at high temperature and pressure conditions to recover most of the unconverted oil (UCO) components in the liquid phase (stream 13). Vapor leaves separator 40 overhead in line 22, and heat is exchanged with hydrogen stream 31 in exchanger 25. Stream 22, which is made up of more than 85 wt % diesel and lighter material, preheats the fractionator feed (not shown in the FIGURE) and generates high pressure steam. Stream 22 is finally cooled to about 200°C in the hot high pressure separator vapor/recycle gas exchanger 25. Stream 22 is then flashed in hot high pressure separator 50. At these relatively high pressure and low temperature conditions, most of the hydrotreated jet and diesel range material is recovered as liquid stream 27 at high pressure, which is pumped (pump 35) to the feedstream (stream 11), which passes to hydrocracking reactor 20 for further processing. The overhead vapor from the hot high pressure separator 50, stream 23, is then cooled in an air cooler (not shown) before entering a cold high pressure separator (not shown). The overhead vapor stream, stream 23, comprises hydrogen, ammonia, and hydrogen sulfide, along with light gases and naphtha. In the cold high pressure separator (not shown) hydrogen, hydrogen sulfide, and light hydrocarbonaceous gases are removed overhead, ammonia is removed from the cold high pressure separator as ammonium bisulfide in the sour water stripper. Naphtha and middle distillates are passed to fractionation.

[0038] Stream 13 passes to hot low pressure separator 60, where it is flashed. Vapor is removed as stream 28. The hot low pressure separator bottoms are removed as stream 73 and passed to UCO (unconverted oil) stripper 30. The material of stream 73 is stream stripped in stripper 30 to recover any lighter material in the UCO stream. Lighter material is removed as stream 26. Jet and diesel range material is withdrawn as a side draw 17 from the column. Side draw 17 combines with stream 19, stripper bottoms 16 (UCO) to become stream 19. A side stream 18 may be taken from bottoms stream 16. Stream 19, recycle oil, is pumped, via pump 45, to storage drum 70. The recycle oil exits storage drum 70 through stream 21 and is pumped, by means of pump 55, to stream 11. Stream 11 is heated in exchanger 15 prior to entering hydrocracking reactor 20 for further aromatic saturation. The overhead liquid stream 26 from the UCO stripper 30 is sent to the main product stripper, and the offgas is sent to fuel gas (not shown).

[0039] The hydrotreated, stripped UCO (stream 16) from the bottom of the UCO stripper, is an excellent quality FCC feed. At this point, a part of stripped unconverted oil (stream 18) is sent out as FCC feed. Further saturation of the FCC feed is thus avoided. Only a limited portion of the UCO (mixed with stream 19), is passed to hydrocracker 20 for further saturation of aromatic components and conversion to distillate products. The amount recycled back is based on the desired overall conversion level.

[0040] The second stage hydrocracking reactor 20 is loaded with hydrocracking catalyst and operates under a clean environment (no heteroatoms), ideally selectively converting the UCO to desired products and further saturating the aromatic components to achieve required jet and diesel properties at different conversion levels. Stream 32 is a sidestream from stream 1. From stream 32, streams 7 and 8 add hydrogen in between the first and second beds and second and third beds of reactor 20 respectively.

[0041] Both the hydrotreating reactor 10 and hydrocracking reactor 20 are designed for the maximum conversion desired. During lower conversion operation, the hydrotreating reaction is maintained at the same temperature as the highest conversion case in order to achieve target denitrification and desulfurization. The temperature of the hydrocracking reactor is reduced at lower conversions.

[0042] The effluent (stream 72) of second stage hydrocracking reactor 20 is cooled (in exchanger 15) to preheat second stage reactor feed (stream 11) fractionator feed and cold low pressure separator liquid stream. Stream 72, now renumbered stream 74, combines with high pressure separator vapor stream 23 for further cooling and the removal of high pressure recycle gas. The hydrocarbon liquid from the cold high pressure separator (not shown) is sent to the fractionation section (not shown) for product recovery.

EXAMPLE

[0043] The following table highlights the advantages of the process scheme of this invention over a conventional process scheme for a 65,000 BPD (barrel per operating day) hydrocracking unit: The table indicates that there is no need in the current invention for post treatment in order to reach desired product specifications. Furthermore, less hydrogen is consumed in the scheme of the current invention than in the conventional case.

<table>
<thead>
<tr>
<th>Process Scheme</th>
<th>New Process Scheme</th>
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<tbody>
<tr>
<td>Process Scheme</td>
<td>Single Stage Once-Through</td>
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<tr>
<td>Fresh Feed Rate, BPSD</td>
<td>65,000</td>
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<tr>
<td>Overall LHSV, 1 hr</td>
<td>0.7-0.9</td>
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<tr>
<td>Product Yield</td>
<td>Base</td>
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<tr>
<td>Jet &amp; Diesel Quality</td>
<td>Needs post treatment for aromatic saturation at low conversion</td>
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<tr>
<td>Chemical H₂ Consumption</td>
<td>Base</td>
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What is claimed is:

1. A method for hydroprocessing a hydrocarbon feedstock, said method employing multiple hydroprocessing zones within a single reaction loop, each zone having one or more catalyst beds, comprising the following steps:
   (a) passing a hydrocarbonaceous feedstock to a first hydroprocessing zone having one or more beds containing hydroprocessing catalyst, the hydroprocessing zone being maintained at hydroprocessing conditions, wherein the feedstock is contacted with catalyst and hydrogen;
   (b) passing the effluent of step (a) directly to a hot high pressure separator, wherein the effluent is separated to produce a vapor stream comprising hydrogen, hydrocarbonaceous compounds boiling at a temperature below the boiling range of the hydrocarbonaceous feedstock, hydrogen sulfide and ammonia and a liquid stream comprising hydrocarbonaceous compounds boiling approximately in the range of said hydrocarbonaceous feedstock;
   (c) passing the vapor stream of step (b) after cooling and partial condensation, to a second hot high pressure separator where it is flashed, thereby producing an overhead vapor stream and a liquid stream, wherein the liquid stream, which comprises hydrotreated hydrocarbons in the middle distillate range, is passed to a second hydroprocessing zone;
   (d) passing the overhead vapor stream from the hot high pressure separator of step (c), after cooling and contact with water, said vapor stream comprising hydrogen, ammonia, hydrogen sulfide, light gases and naphtha, to a cold high pressure separator, wherein hydrogen, hydrogen sulfide, and light hydrocarbonaceous gases are removed overhead, ammonia is removed from the cold high pressure separator as ammonium bisulfide in the sour water stripper, and naphtha and middle distillates are passed to fractionation;
   (e) passing the liquid stream from the hot high pressure separator of step (b) to a hot low pressure separator, where it is flashed to produce an overhead stream comprising gases and a liquid stream comprising unconverted oil;
   (f) passing the liquid stream of step (e) which comprises unconverted oil, to a steam stripper, where a vapor stream is removed overhead and a liquid stream, which comprises stripped unconverted oil, is recovered.

2. The process of claim 1, wherein at least a portion of the stripped unconverted oil of step (f) is passed to a fluid catalytic cracking unit as feed.

3. The process of claim 1, wherein at least a portion of the stripped unconverted oil of step (f) is combined with the liquid effluent of step (c) to form a liquid stream which is passed to the second hydroprocessing zone.

4. The process of claim 1, wherein the second hydroprocessing zone contains at least one bed of hydroprocessing catalyst suitable for aromatic saturation and ring opening.

5. The process of claim 4, wherein the liquid stream is contacted under hydroprocessing conditions with the hydroprocessing catalyst, in the presence of hydrogen to produce middle distillate products.

6. The process of claim 1, wherein the hydroprocessing conditions of step (a) comprise a reaction temperature of from 400° F-950° F (204° C-510° C), a reaction pressure in the range from 500 to 5000 psig (3.5-34.5 MPa), an LHSV in the range from 0.1 to 15 hr-1 (v/v), and hydrogen consumption in the range from 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m³ H₂/m³ feed).

7. The process of claim 6, wherein the hydroprocessing conditions of step 1(a) preferably comprise a temperature in the range from 650° F-850° F (343° C-454° C), reaction pressure in the range from 1500-3500 psig (10.4-24.2 MPa), an LHSV in the range from 0.25 to 2.5 hr-1, and hydrogen consumption in the range from 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m³ H₂/m³ feed).

8. The process of claim 1, wherein the hydroprocessing conditions of step 1(e) preferably comprise a temperature in the range from 400° F-950° F (204° C-510° C), a reaction pressure in the range from 500 to 5000 psig (3.5-34.5 MPa), an LHSV in the range from 0.1 to 15 hr-1 (v/v), and hydrogen consumption in the range from 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m³ H₂/m³ feed).

9. The process of claim 9, wherein the hydroprocessing conditions of step 1(e) preferably comprise a temperature in the range from 650° F-850° F (343° C-454° C), reaction pressure in the range from 1500-3500 psig (10.4-24.2 MPa), an LHSV in the range from 0.25 to 2.5 hr-1, and hydrogen consumption in the range from 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m³ H₂/m³ feed).

10. The process of claim 1, wherein the feed to step 1(a) comprises hydrocarbons boiling in the range from 500° F to 1500° F.

11. The process of claim 1, wherein the feed is selected from the group consisting of vacuum gas oil, heavy atmospheric gas oil, delayed coker gas oil, visbreaker gas oil, FCC light cycle oil, and deasphalted oil.

12. The process of claim 1, wherein the hydroprocessing catalyst comprises both a cracking component and a hydrogenation component.

13. The process of claim 12, wherein the hydrogenation component is selected from the group consisting of Ni, Mo, W, Pt and Pd or combinations thereof.

14. The process of claim 3, wherein the cracking component may be amorphous or zeolitic.

15. The process of claim 11, wherein the zeolitic component is selected from the group consisting of Y, USY, REX, and REY zeolites.

16. The process of claim 1, wherein the middle distillate products produced do not require additional treatment to meet product specifications.

17. The process of claim 16, wherein the sulfur content of jet fuel is less than 10 ppm, the smoke point is greater than 24 mm, the sulfur content of diesel is less than 10 ppm, and the cetane index is greater than 50.

18. The process of claim 1, in which smaller amounts of hydrogen are used than in single stage once-through hydrocracking.

19. The process of claim 18, wherein the amount of hydrogen used is 160 SCF per barrel lower than the amount used in single stage once-through hydrocracking at 60% conversion, 100 SCF per barrel lower than the amount used in single stage once-through hydrocracking at 80% conversion, and 50 SCF per barrel lower than the amount used in single stage once-through hydrocracking at 90% conversion.

20. The process of claim 1, wherein the hydrotreating occurs in the first reaction zone and hydrocracking occurs in the second reaction zone.