

INTEGRATED HYDROCONVERSION PROCESS
WITH REVERSE HYDROGEN FLOW



166166

FIELD OF THE INVENTION

The present invention relates to the field of hydroprocessing. In particular, the present invention relates to hydroprocessing to obtain high conversions, product selectivity and selective hydrotreating of specific boiling range products.

BACKGROUND OF THE INVENTION

Much of refinery processing involves reaction of refinery streams in a hydrogen atmosphere. In order to maximize conversion efficiencies and to maintain catalyst life, excess hydrogen is generally used in the catalytic conversion processes, with the unreacted hydrogen being recovered, purified and repressurized for use as a recycle stream. Such recycle processes are costly, both in energy and in equipment. Some progress has been made in developing methods for using a single hydrogen loop in a two-stage reaction process.

U.S. Pat. No. 5,009,768 teaches hydrodemetallizing a high-residual vacuum gas oil and hydroconverting the product from the first reaction zone at deep denitrogenation conditions in a second reaction zone. A cycle oil from an FCC may be added to the feed to the second reaction zone. U.S. Pat. No. 4,283,271 and U.S. Pat. No. 4,283,272 teach a processes for making lubricating oil which include passing a suitable hydrocarbon feed and hydrogen sequentially through a hydrocracking zone, a catalytic dewaxing zone and a hydrotreating zone, all at high pressure and in that order, with purification of the hydrogen gas prior to passage to the dewaxing zone. EP 787787 teaches hydroprocessing in parallel reactors, while hydrogen flows in series between the reactors.

U.S. Pat. No. 3,328,290 to Hengstebeck teaches combining the effluent from a hydrocracking zone with a hydrocarbon feedstock and passing the resultant combined stream through a feed-preparation zone.- A heavier liquid effluent, from the liquid effluent from the feed preparation zone, is passed, along with a separated hydrogen-containing gas, to the hydrocracking zone. Hengstebeck does not teach feeding a separate VGO stream to the hydrocracking zone.

Other methods have been proposed for separating partially reacted reactants within a reactor, removing one of the reacting streams (generally either a liquid or a vapor stream) and continuing reaction of the remaining stream. For example, U.S. Pat. No. 3,172,836 teaches a two-stage hydrocracking process, with denitrification being accomplished in the first conversion zone and cracking conversion being accomplished in the second conversion zone. In U.S. Pat. No. 3,172,836, a liquid-vapor separation zone is located between two catalyst beds for withdrawing a normally gaseous fraction and a normally liquid fraction from a first catalyst bed. The normally gaseous fraction, along with a second normally liquid



fraction, is then passed downwardly through a second catalyst bed. The normally liquid fraction passed through the second catalyst bed may be a liquid fraction recovered from a distillation of the effluent from the first catalyst bed. In U.S. Pat. No. 4,615,789 a liquid/vapor separator is utilized between catalyst beds to remove
5 liquid from between the beds and permit vapor separated by the separator to pass through catalyst beds below the separator.

U.S. Pat. No. 5,603,824 teaches a reactor having at least a top bed containing a hydrocracking catalyst and a bottom bed containing a dewaxing catalyst. A
10 hydrocarbon feed mixture is separated, with the heavier stream being hydrocracked in the top bed of the reactor and the lighter stream combined with the effluent from the top bed and the combination catalytically dewaxed in the bottom bed.

15 However, additional developments are needed for hydroconverting dissimilar refinery streams using a single hydrogen source. The present invention is directed to such a process.

20

SUMMARY OF THE INVENTION

In one aspect, the invention provides a method for reducing the number of reactor vessels required for hydroprocessing in a refinery. In another aspect, the invention provides a method for hydroprocessing
25 two refinery streams using a single hydrogen supply and a single hydrogen recovery system. In another aspect, the present invention provides a method for hydrocracking a refinery stream and hydrotreating a second refinery stream in a common reactor and with a common hydrogen feed supply without poisoning the feed to the hydrocracking reaction zone with contaminants present in the feed to the hydrotreating reaction zone. In another aspect, the present invention is
30 directed to hydroprocessing two or more dissimilar refinery streams in an integrated hydroconversion process while maintaining good catalyst life and high yields of the desired products, particularly distillate range refinery products. Such dissimilar refinery streams may originate from different refinery processes, such as
35 a VGO, derived from the effluent of a VGO hydrotreater, which contains relatively few catalyst contaminants and/or aromatics, and an FCC cycle oil or straight run diesel, which contains substantial amounts of aromatic compounds.

40 The integrated hydroconversion process comprises combining a first refinery stream with a first hydrogen-rich gaseous stream to form a first feedstock; passing the first feedstock to a first reaction zone maintained at conditions sufficient to effect a boiling range conversion, to form a first reaction zone effluent comprising normally liquid phase components and normally gaseous phase components;
45 combining the entire first reaction zone effluent with a second refinery stream, having a boiling point range below the boiling point range of the first refinery

stream, to form a second feedstock; passing the second feedstock to a second reaction zone maintained at conditions sufficient for converting at least a portion of the aromatics present in the second refinery stream, to form a second reaction zone effluent; separating the second reaction zone effluent into at least one
5 distillate fraction and a second hydrogen-rich gaseous stream; and recycling at least a portion of the second hydrogen-rich gaseous stream to the first reaction zone.

10 A VGO is a preferred first refinery stream, and a synthetic or straight run middle distillate is a preferred second refinery stream. A suitable synthetic middle distillate, formed by cracking a heavier stock, may contain high nitrogen levels. The second refinery stream generally boils in the middle distillate boiling range, and is hydrotreated to remove nitrogen and/or aromatics, without excessive cracking. The preferred first reaction zone contains hydrocracking catalyst,
15 maintained at hydrocracking conditions. Likewise, the preferred second reaction zone contains hydrotreating catalyst, maintained at hydrotreating reaction conditions. In the process, the first and the second reaction zones are contained within a single reactor vessel, or in two close coupled reactor vessels, with an single integrated hydrogen supply and recovery system serving both reaction
20 zones. The process serves to prevent contaminants present in the second refinery stream from fouling the catalyst in the first reaction zone.

A preferred process comprises combining a VGO stream with a first hydrogen-rich gaseous stream to form a first feedstock; passing the first feedstock to a
25 hydrocracking reaction zone, maintained at hydrocracking conditions sufficient to effect a boiling range conversion, to form a hydrocracking reaction zone effluent comprising normally liquid phase components and normally gaseous phase components; combining the entire hydrocracking reaction zone effluent, at substantially the same temperature and at substantially the same temperature as
30 the hydrocracking reaction zone, with a second refinery stream, having a boiling point range below the boiling point range of the first refinery stream, to form a second feedstock; passing the second feedstock to a hydrotreating reaction zone, maintained at hydrotreating conditions sufficient for converting at least a portion of the nitrogen compounds and at least a portion of the aromatic compounds present
35 in the residuum stream, to form a hydrotreating reaction zone effluent; separating the hydrotreating reaction zone effluent into at least a liquid stream and a second hydrogen-rich gaseous stream; separating the liquid stream to recover at least one middle distillate stream; and recycling at least a portion of the second hydrogen-rich gaseous stream to the hydrocracking reaction zone.

40

IN THE FIGURES

Figs. 1 and 2 show embodiments of the invention with two reaction zones in a single reactor vessel. Figs. 3 and 4 show embodiments of the invention with reaction zones in separate vessels, and a separation zone between the vessels.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to two reaction processes, using two dissimilar feeds, which are combined into a single integrated reaction process, using a single hydrogen supply and recovery system. The reactant and product flows and reaction conditions in the present process are selected to avoid contaminating catalysts or products while maintaining catalyst performance and process efficiencies. The feeds to the process include a first refinery stream containing relatively lesser amounts of aromatics, including multi-ring aromatics such as asphaltenes, and a second refinery stream which contains relatively greater amounts of aromatics and multi-ring aromatics. The process is particularly useful for treating a relatively clean feedstock under cracking conditions and a more aromatic feed under treating conditions in an integrated process, using a single hydrogen supply and recovery system, without fouling the cracking catalysts with the contaminants in the second refinery stream or without overcracking the second refinery stream.

A suitable first refinery stream is a VGO boiling in a temperature range above about 500°F. (260°C), usually within the temperature range of 500°-1100°F. (260-593°C.). The first refinery stream may contain nitrogen, usually present as organonitrogen compounds, in amounts greater than 1 ppm. It is a feature of the present process that feeds with high levels of nitrogen and sulfur, including those containing up to 0.5 wt% (and higher) nitrogen and up to 2 wt% and higher sulfur may be treated in the present process. Preferred feed streams for the first reaction zone contain less than about 200 ppm nitrogen and less than 0.25 wt% sulfur. The first refinery stream is also preferably a low aromatic stream, including multi-ring aromatics and asphaltenes. Suitable first refinery streams, including feedstocks to the first reaction zone which may contain recycle streams, contain less than about 500 ppm asphaltenes, preferably less than about 200 ppm asphaltenes, and more preferably less than about 100 ppm asphaltenes. Example first refinery streams include light gas oil, heavy gas oil, vacuum gas oil, straight run gas oil, deasphalted oil, and the like. The first refinery stream may have been processed, e.g. by hydrotreating, prior to the present process to reduce or substantially eliminate its heteroatom content. The first refinery stream may also comprise recycle components.

The first reaction step removes nitrogen and sulfur from the first refinery stream in the first reaction zone and effects a boiling range conversion, so that the normally liquid portion of the first reaction zone effluent has a normal boiling range below the normal boiling point range of the first refinery feedstock. By "normal" is meant a boiling point or boiling range

based on a distillation at one atmosphere pressure, such as that determined in a D1160 distillation. Unless otherwise specified, all distillation temperatures listed herein refer to normal boiling point and normal boiling range temperatures. The process in the first reaction zone may be controlled to a certain cracking conversion or to a desired product sulfur level or nitrogen level or both. Conversion is generally related to a reference temperature, such as, for example, the minimum boiling point temperature of the feedstock. The extent of conversion relates to the percentage of feed boiling above the reference temperature which is converted to products boiling below the reference temperature.

The first reaction zone effluent includes normally liquid phase components, e.g. reaction products and unreacted components of the first refinery stream which are liquids at ambient conditions, and normally gaseous phase components, e.g. reaction products and unreacted hydrogen, which are normally vapors at ambient conditions. In the process, the first reaction zone is maintained at conditions sufficient to effect a boiling range conversion of the first refinery stream of at least about 25%, based on a 650°F reference temperature. Thus, at least 25% by volume of the components in the first refinery stream which boil above about 650°F are converted in the first reaction zone to components which boil below about 650°F. Operating at conversion levels as high as 100% is also within the scope of the invention. Example boiling range conversions are in the range of from about 30% to 90% by volume or from about 40% to 80% by volume. The first reaction zone effluent is further decreased in nitrogen and sulfur content, with at least about 50% of the nitrogen containing molecules in the first refinery stream being converted in the first reaction zone. Preferably the normally liquid products present in the first reaction zone effluent contain less than about 1000 ppm sulfur and less than about 200 ppm nitrogen, more preferably less than about 250 ppm sulfur and about 100 ppm nitrogen.

Reaction conditions in the first reaction zone include a reaction temperature between about 250°C and about 500°C (482°-932°F.), pressures from about 3.5 MPa to about 24.2 MPa (500-3,500 psi), and a feed rate (vol oil/vol cat h) from about 0.1 to about 20 hr⁻¹. Hydrogen circulation rates are generally in the range from about 350 std liters H₂/kg oil to 1780 std liters H₂/kg oil (2,310-11,750 standard cubic feet per barrel). Preferred reaction temperatures range from about 340°C to about 455°C (644°-851°F.). Preferred total reaction pressures range from about 7.0 MPa to about 20.7 MPa (1,000-3,000 psi). With the preferred catalyst system, it has been found that preferred process conditions include contacting a petroleum feedstock with hydrogen under hydrocracking conditions comprising

a pressure of about 13.8 MPa to about 20.7 MPa (2,000-3000 psi), a gas to oil ratio between about 379-909 std liters H₂/kg oil (2,500-6,000 scf/bbl), a LHSV of between about 0.5-1.5 hr⁻¹, and a temperature in the range of 360°C. to 427°C (680°-800°F.).

The first and second reaction zones contain one or more catalysts. If more than one
5 distinct catalyst is present in either of the reaction zones, they may either be blended or be present as distinct layers. Layered catalyst systems are taught, for example, in U.S. Patent No. 4,990,243, the disclosure of which is incorporated herein by reference for all purposes. Hydrocracking catalysts useful for the first reaction zone are well known. In general, the hydrocracking catalyst comprises a cracking component and a hydrogenation component on
10 an oxide support material or binder. The cracking component may include an amorphous cracking component and/or a zeolite, such as a Y-type zeolite, an ultrastable Y type zeolite, or a dealuminated zeolite. A suitable amorphous cracking component is silica-alumina.

The hydrogenation component of the catalyst particles is selected from those elements known to provide catalytic hydrogenation activity. At least one metal component selected
5 from the Group VIII (IUPAC Notation) elements and/or from the Group VI (IUPAC Notation) elements are generally chosen. Group V elements include chromium, molybdenum and tungsten. Group VIII elements include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The amount(s) of hydrogenation component(s) in the catalyst suitably range from about 0.5% to about 10% by weight of Group VIII metal
0 component(s) and from about 5% to about 25% by weight of Group VI metal component(s), calculated as metal oxide(s) per 100 parts by weight of total catalyst, where the percentages by weight are based on the weight of the catalyst before sulfiding. The hydrogenation components in the catalyst may be in the oxidic and/or the sulphidic form. If a combination of at least a Group VI and a Group VIII metal component is present as (mixed) oxides, it will
5 be subjected to a sulfiding treatment prior to proper use in hydrocracking. Suitably, the catalyst comprises one or more components of nickel and/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium. Catalysts containing nickel and molybdenum, nickel and tungsten, platinum and/or palladium are particularly preferred.

0 The hydrocracking catalyst particles of this invention may be prepared by blending, or co-mulling, active sources of hydrogenation metals with a binder. Examples of suitable binders include silica, alumina, clays, zirconia, titania, magnesia and silica-alumina. Preference is given to the use of alumina as binder. Other components, such as phosphorous,

may be added as desired to tailor the catalyst particles for a desired application. The blended components are then shaped, such as by extrusion, dried and calcined to produce the finished catalyst particles. Alternative, equally suitable methods of preparing the amorphous catalyst particles include preparing oxide binder particles, such as by extrusion, drying and calcining, followed by depositing the hydrogenation metals on the oxide particles, using methods such as impregnation. The catalyst particles, containing the hydrogenation metals, are then further dried and calcined prior to use as a hydrocracking catalyst.

The effluent from the first reaction zone comprises normally liquid phase components and normally gaseous phase components. The normally gaseous phase components includes unreacted hydrogen from the first reaction zone. In conventional processing, the reaction zone effluent is normally separated in one or more separation zones, operated at decreasing temperature and/or pressure, in order to recover a substantially pure hydrogen stream for recycle. It is a feature of the present process that normally gaseous phase components are passed to the second reaction zone at substantially the same pressure as the first reaction zone and without substantial cooling. In one embodiment of the invention, the entire effluent from the first reaction zone is passed, without cooling and without additional separation to the second reaction zone. In a second embodiment, the first reaction zone effluent is separated at substantially the same pressure and the same temperature as the first reaction zone, and at least a portion of the separated gaseous phase is passed to the second reaction zone without additional cooling, other than the cooling which might occur if the separated gas phase is blended with other relatively cooler reactants. In a third embodiment, the first reaction zone effluent is separated in a first separation zone, and at least a portion of normally gaseous phase components are passed, without substantial cooling, for blending with a second refinery stream. Such separation may occur within the reactor containing one of the reaction zones, or in a separation zone distinct from reaction vessels.

Thus, unreacted hydrogen from the first reaction zone is combined with a second refinery stream, and the combined feedstock, along with optionally added hydrogen containing gas, is cascaded to a second catalyst bed in a second reaction zone, which is maintained at hydrotreating conditions sufficient to remove at least a portion of the nitrogen and a portion of the aromatic compounds from the second refinery stream. The feedstocks may flow through one or both of the reaction zones in gravity flow in a downwardly direction or upwardly against gravity.

The second reaction step is for hydrotreating a second refinery stream at conditions sufficient to remove at least a portion of the aromatic compounds. Preferably, at least about 50% of the aromatics are removed from the second refinery stream in the integrated process. Typical hydrotreating functions also include removing heteroatoms such as sulfur and
5 nitrogen, removing metals contained in the feed, and saturating at least some of the olefins in the feed. It is particularly desirable to remove multi-ring aromatic materials during hydrotreating, as they are particularly prone to fouling a hydrocracking catalyst which they might contact. A measure of cracking conversion may also occur, depending on the severity of the hydrotreating conditions.

0 An example second refinery stream has a boiling point range which is higher than that of the first refinery stream, and contains a larger amount of sulfur, nitrogen and aromatic impurities, especially multi-ring aromatics. Suitable second refinery streams include deasphalted residua or crude, crude oil atmospheric distillation column bottoms (reduced crude oil or atmospheric column residuum), or vacuum distillation column bottoms (vacuum
5 residua). A deasphalted oil is also a suitable second refinery stream. A residuum feedstock which may be treated in the present process is a high boiling hydrocarbonaceous material having a normal boiling range mostly above 316°C (600°F), or wherein at least 80% v/v of the feed boils between 316°C and 816°C (600°-1500°F, and preferably that at least about 50 vol% of the second refinery stream has a normal boiling point temperature of greater than
about 538°C (1000°F). The residuum feedstock further contains a high concentration of asphaltenes, making it a generally unacceptable feedstock for hydrocracking without a preliminary hydrotreating step. Asphaltenes may suitably be determined as the normal-heptane insolubles content per ASTM D3279-90.

In the normal-heptane insolubles determination, approximately 1.0 grams of a refinery stream sample is mixed with n-heptane in the ratio of 100 mL of solvent per 1 gram of sample. The mixture is gently refluxed for a period of 15-20 minutes and then allowed to cool for 1 hour. The sample is then warmed to 38°-49°C and filtered through a prepared filter pad which has been pre-wet with 5 mL of n-heptane. The precipitate is washed with three portions of 10 mL of n-heptane, dried at 107°C for 15 minutes, cooled and weighed. The mass percent of normal-heptane insolubles is determined as a percentage by weight of the original sample.

Feedstocks usefully processed in the present invention are those containing more than about 500 ppm asphaltenes, and up to as much as 10,000 ppm asphaltenes or more; and

further containing more than 10 ppm metals and more than 0.1% by weight sulfur, typically more than 1 wt% sulfur and 0.2 wt% nitrogen, and more than 50 % aromatics. The metals are believed to be present as organometallic compounds, but the concentrations of metals referred to herein are calculated as parts per million pure metal. The contaminating metals in the feed typically include nickel, vanadium and iron. The sulfur is present as organic sulfur compounds and the wt% sulfur is calculated based on elemental sulfur. The residuum feedstock will typically have higher sulfur and nitrogen contents than the feedstock to the first reaction zone. In this example process, the second refinery stream is hydrotreated to remove nitrogen, sulfur and metal impurities from the feedstock and to saturate or otherwise remove aromatics, including heavy aromatics. Such impurities, especially heavy aromatics and metals, deactivate a hydrocracking catalyst at an unacceptably rapid rate, were the first and second refinery streams combined and contacted together with hydrogen over the hydrocracking catalyst. Furthermore, in the process, unreacted or incompletely reacted products remaining in the effluent from the second reaction zone are effectively isolated from the first reaction zone to further prevent contamination of the catalyst contained therein. The second refinery stream may have been hydrotreated or demetallized prior to being used as the feedstock for the present process.

When the above-described process is used to hydrotreat feedstocks to remove sulfur and nitrogen impurities, hydrotreating conditions typically used in the second reaction zone will include a reaction temperature between about 250°C and about 500°C (482°-932°F), pressures from about 3.5 MPa to about 24.2 MPa (500-3,500 psi), and a feed rate (vol oil/vol cat h) from about 0.1 to about 20 hr⁻¹. Hydrogen circulation rates are generally in the range from about 350 std liters H₂/kg oil to 1780 std liters H₂/kg oil (2,310-11,750 standard cubic feet per barrel). Preferred reaction temperatures range from about 340°C to about 455°C (644°-851°F.). Preferred total reaction pressures range from about 7.0 MPa to about 20.7 MPa (1,000-3,000 psi).

The hydrotreating catalyst for the beds will typically be 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 hydrotreating catalysts are alumina supported cobalt-molybdenum, nickel sulfide, nickel-tungsten, cobalt-tungsten and nickel-molybdenum. Typically such hydrotreating catalysts are presulfided.

The subject process is especially useful in the production of middle distillate fractions boiling in the range of about 121°-371°C. (250°-700°F.) as determined by the appropriate

ASTM test procedure. By a middle distillate fraction having a boiling range of about 121°-371°C. (250°-700°F) is meant that at least 75 vol%, preferably 85 vol%, of the components of the middle distillate have a normal boiling point of greater than about 121°C. (250°F.) and furthermore that at least about 75 vol%, preferably 85 vol%, of the components
5 of the middle distillate have a normal boiling point of less than 371°C. (700°F.). The term "middle distillate" is intended to include the diesel, jet fuel and kerosene boiling range fractions. The kerosene or jet fuel boiling point range is intended to refer to a temperature range of about 138°-274°C. (280°-525°F.) and the term "diesel boiling range" is intended to refer to hydrocarbon boiling points of about 121°-371°C. (250°-700°F.). Gasoline or naphtha
10 is normally the C₅ to 204°C. (400°F.) endpoint fraction of available hydrocarbons. The boiling point ranges of the various product fractions recovered in any particular refinery will vary with such factors as the characteristics of the crude oil source, refinery local markets, product prices, etc. Reference is made to ASTM standards D-975 and D-3699-83 for further details on kerosene and diesel fuel properties.

15 In the process a single hydrogen supply provides hydrogen for both the first and second reaction zones. Make-up hydrogen is combined with low pressure recycle hydrogen from the second reaction zone, and the combination passed to the first reaction zone. Unreacted hydrogen from the first reaction zone is passed without substantial cooling to the second reaction zone. In contrast to conventional processes in which the unreacted hydrogen
20 from the first reaction zone is separated from the reaction zone effluent, cooled, depressurized and purified to remove contaminants, at least a portion of the unreacted hydrogen in the present invention is passed from the first reaction zone to the second reaction zone at substantially the same pressure as the first reaction zone and without additional cooling, except for the incidental pressure and temperature losses incurred during separation
5 and in conducting the effluent from the first reaction zone to the second reaction zone. The preferred temperature of the unreacted hydrogen which is passed from the first to the second reaction zones is at least about 177°C (350°F), more preferably at least about 260°C (500°F) and most preferably at least about 371°C (650°F). Unreacted hydrogen from the second reaction zone is purified to remove contaminants and recycled to the first reaction zone.

0 Reference is now made to the figures, which disclose preferred embodiments of the invention. Not included in the figures are the various pieces of auxiliary equipment such as heat exchangers, condensers, pumps and compressors, which, of course, would be necessary

for a complete processing scheme and which would be known and used by those skilled in the art.

In Fig. 1, a single, downflow reactor vessel 80 contains at least two vertically aligned reaction zones. A first reaction zone 115 is for cracking a first refinery stream 85. A second
5 reaction zone 20 is for removing nitrogen-containing and aromatic molecules from a second refinery stream 5. A suitable volumetric ratio of the catalyst volume in the first reaction zone to the catalyst volume in the second reaction zone encompasses a broad range, depending on the ratio of the first refinery stream to the second refinery stream. Typical ratios generally lie between 20:1 and 1:20. A preferred volumetric range is between 10:1 and 1:10. A more
10 preferred volumetric ratio is between 5:1 and 1:2.

In the integrated process, a first refinery stream 85 is combined with a first gaseous feed stream 170 to form a first feedstock 105 which is heated in first feed furnace 110 and passed to first reaction zone 115 contained within reactor vessel 80. First gaseous feed
15 stream 170 contains greater than 50% hydrogen, the remainder being varying amounts of light gases, including hydrocarbon gases. First gaseous feed stream 170 shown in the figure is a blend of make-up hydrogen 95 and recycle hydrogen 175. While the use of a recycle hydrogen stream is generally preferred for economic reasons, it is not required. In the process, the first feedstock 105 is passed to the first reaction zone 115 at conditions sufficient to effect a boiling range conversion, to form a first reaction zone effluent 120 comprising
20 normally liquid phase components and normally gaseous phase components

In an alternative embodiment, the second reaction step is for hydrotreating a low boiling refinery stream to reduce the aromatic content of a second refinery stream without overcracking. A substantial portion of this light feed boils in a temperature range below the temperature range of the first refinery stream, and generally in the middle distillate range or
5 slightly higher, so that the process of hydrotreating in the second reaction zone produces substantial amounts of high quality middle distillate fuels. Thus, at least about 75 vol% of a suitable second refinery stream has a normal boiling point temperature of less than about 538°C (1000°F). A refinery stream with at least about 75% v/v of its components having a normal boiling point temperature within the range of 250°-700°F in an example of a
0 preferred second refinery stream. The process provides a method for hydrotreating a second refinery stream containing a larger amount of aromatics than the first refinery stream. Suitable second refinery streams include straight run middle distillate streams from a crude fractionation unit, including straight run diesel; synthetic cracked stocks such as cracked

products from an FCC or a coker, including light and heavy cycle oil and coker gas oil; deasphalted oil; VGO streams from a synthetic fuel process and the like. While a substantial portion of the second refinery stream may boil in the middle distillate range, so that additional molecular weight reduction by cracking is unnecessary and even undesirable, the feed to the second reaction zone generally contains high amounts of aromatics or olefins, which contribute to undesirable middle distillate fuel properties if they are not removed. Indeed, the aromatic components in the second refinery streams may inhibit the activity of the hydrocracking catalyst were the hydrocracking catalyst contacted with the second refinery stream. The present invention is thus based on the surprising discovery that catalytic cracking activity for boiling point reduction increases, hydrogen consumption improves (i.e. is reduced), and middle distillate yields increase when the first refinery stream and the second refinery stream are introduced as separate streams, to different locations in the integrated hydroconversion process, rather than being mixed and passed together through both the first and the second reaction zones. When light feeds are employed as the second refinery stream, an optional bottoms recycle stream to the first reaction zone will contain substantially no unreacted components of the second refinery stream.

In Fig. 1 and Fig. 2, first reaction zone effluent **120** is passed to interstage region **125**, a region in the reactor vessel which contains means for mixing and redistributing liquids and gases from the reaction zone above before they are introduced into the reaction zone below. Such mixing and redistribution improves reaction efficiency and reduces the chances of thermal gradients or hot spots in the reaction zone below. In the process, second refinery stream **5**, is combined with optional hydrogen containing stream **140** forming combined feedstock **15**, which is heated in second feed furnace **10** and passed to the interstage region **125**. Hydrogen added in stream **140** restores the hydrogen reacted in the first reaction zone, and is not required if sufficient hydrogen is added through stream **170** to the first reaction zone. While stream **140** may include recycled hydrogen, it may also include make-up hydrogen, depending on the hydrogen availability at a particular process location. In the embodiment shown in the drawing in Fig. 1, the entire first reaction zone effluent is passed for combination with the combined, second feedstock **15** at substantially the same temperature and at substantially the same pressure as the first reaction zone. In the embodiment illustrated in Fig. 2, the normally liquid phase components are separated from the normally gaseous phase components in the interstage region. The entire vapor stream **130**

is passed without substantial cooling to the second reaction zone **20** for supplying at least a portion of the hydrogen for reaction of second feedstock **15**.

The second feedstock **15**, in combination with at least a portion of the effluent from the first reaction zone, is passed to second reaction zone **20**, maintained at conditions
5 sufficient for converting at least a portion of the aromatics present in the second refinery stream, to form a second reaction zone effluent. Since the first reaction zone effluent is already relatively free of the contaminants to be removed in the second reaction zone, the first reaction zone effluent passes largely unchanged through the second reaction zone. However, according to the invention, the presence of the first reaction zone effluent plays an important
10 and unexpected economic benefit in the integrated process. Leaving the first reaction zone, the effluent carries with it substantial thermal energy, which is passed to the second feedstock in the interstage region between the two reaction zones. This permits adding a cooler second stream to the integrated system than would otherwise be required, and saves on furnace and heating costs. As the second feedstock passes through the second reaction zone, the
15 temperature again tends to increase due to exothermic reaction heating in the second reaction zone. Having the liquid first effluent in the second feedstock serves as a heat sink, which moderates the temperature increase through the second reaction zone, and therefore reduces the requirement for quench gas introduction. The heat energy contained in the liquid reaction products leaving the second reaction zone is further available for exchange with other streams
20 requiring heating. Generally, the outlet temperature of the second reaction zone will be higher than the outlet temperature of the first zone. In this case, the current invention will afford the added heat transfer advantage of elevating the temperature of the first reaction zone effluent for more effective heat transfer. The effluent from the first reaction zone also carries the unreacted hydrogen for use in the second reaction zone without any heating or pumping
5 requirement to increase pressure.

Second reaction zone effluent **25** contains unreacted hydrogen, a hydrocarbonaceous component and impurity gases generated during reaction, including hydrogen sulfide and ammonia. The second reaction zone effluent **25** is passed to second separation zone **30**, for separating a liquid product from a normally gaseous product, often in a series of separation
0 units operated at varying pressures and temperatures in order to maximize the efficiency of the separation, and to produce a high purity hydrogen stream. Ammonia and H₂S produced during hydrotreating are removed, typically by water scrubbing, and optionally by scrubbing using a sorbent such as an amine adsorbent. An example separation scheme for a

hydroconversion process is taught in U.S. Patent No. 5,082,551, the entire disclosure of which is incorporated herein by reference for all purposes. The effluent may also be cooled by any conventional means, e.g., by heat exchanger 180. At least a hydrogen rich gaseous stream 150 and a second liquid stream 35 are recovered from the second separation zone 30.

5 The hydrogen rich gaseous stream 150 leaving the second separation zone is relatively free of both hydrogen sulfide and ammonia. A preferred hydrogen rich gaseous stream 150 is cooled and recovered at a temperature in the range of about 38°C to about 149°C (100°-300°F) or preferably in the range of about 38°C to about 93°C (100°F-200°F). The now purified hydrogen rich gaseous stream 150 is repressurized through compressor 160, and distributed
10 to various locations in the process. A portion of stream 150 may be introduced to second reaction zone 20 as a second quench stream 145, added to the second reaction zone to absorb some of the excess heat from the zone generated by the exothermic hydrotreating reactions occurring therein. An additional portion of stream 150 may be introduced to first reaction zone 115 as a first quench stream 155. An additional portion of stream 150 is combined with
5 make-up hydrogen 95 for use in the first reaction zone 115. An additional portion of stream 150 may be introduced to second reaction zone 20 as stream 140 (Figs 1, 2, 3 and 4).

Second liquid stream 35, shown in combination with first liquid stream 135 to form combined liquid product 100 in Fig. 2, is passed to fractionation zone 40, which is typically a
distillation section comprising one or more atmospheric distillation columns and optionally
0 one or more vacuum distillation columns. A light product and at least one liquid product are recovered. Fractionation zone 40, in the preferred embodiment, is operated to produce a number of distillate streams. Five streams are shown in Fig. 1. These include light product 45, light naphtha stream 50, heavy naphtha stream 55, kerosene stream 60 and diesel stream 65. A liquid bottoms stream 70, which contains unreacted and partially reacted products and
5 materials which boil above a target temperature, (e.g. greater than about 260°C/500°F) is also withdrawn. Stream 70 may be recovered as product stream 75 for processing elsewhere, e.g. additional distillation, treating in an FCC unit or a dewaxing unit for making a lubricating oil base stock. At least a portion of stream 70 and/or at least a portion of one of the distillate fractions (i.e. streams 50, 55, 60 or 65) may also be recycled to the first reaction zone 115. A
1) recycle stream 90 is illustrated in Fig. 2.

For treating a residuum as the second refinery stream, it is preferred than neither an atmospheric distillation bottoms product or a vacuum distillation bottoms product be recycled

to the first reaction zone, to avoid contaminating the catalyst contained therein. Rather, a distillate stream may optionally be recycled instead.

Reference is now made to further embodiments, illustrated in Figs. 3 and 4, in which a first reaction zone 115 and a second reaction zone 20 are in separate reactor vessels 80a and 80b, and the interstage region is now a first separation zone 125 separate from the reactor vessels.

Feed to the first reaction zone comprises either one or more refinery streams (e.g. line 85), one or more recycle streams (e.g. lines 90 and 280), or a combination of refinery streams and recycle feed. If used in the process, first refinery stream 85 may be one or a mixture of feeds.

In Fig. 3, first refinery stream 85 is combined with first hydrogen rich gaseous stream 170 to form first feedstock 105, which is heated in feed furnace 110 and passed to first reaction zone 115. Stream 170 is a hydrogen-containing stream derived from recycle hydrogen stream 175, and containing optional make-up hydrogen 95. First reaction zone effluent 120 recovered from the first reaction zone 115 is passed to interstage region 125, which now serves as a first separation zone separate from the reactor vessels. A vapor stream 130 and a first liquid stream 135 are recovered from zone 125.

First separation zone 125, which is preferably a single flash separation unit, is in fluid communication with the second reaction zone 20 and with the first reaction zone 115. Following separation, vapor stream 130 is passed to second reaction zone 20 at substantially the pressure of the first reaction zone and without substantial cooling. It will be recognized that some incidental heat loss occurs in the processing vessels and piping used in passing the vapor stream 130 from the first separation zone 125 to the second reaction zone 20. Vapor stream 130 may further be cooled when blended with other cooler feed streams. However, it is desirable to maintain such heat losses at a minimum, in order to save heating costs when adding the vapor stream 130 to the second reaction zone. A preferred vapor stream 130 is maintained at a temperature of at least about 350°F (177°C), more preferably at least about 500°F (260°C) and most preferably at least about 650°F (371°C), up to the temperature of the first reaction zone.

First separation zone 125 is likewise maintained at a high temperature to minimize heat losses in this vessel. In practice a target first separation temperature is the design temperature for the separation unit, based on the design and metallurgical limit of the materials of construction of the unit. Accordingly, the preferred first separation zone is

maintained at a temperature of at least about 350°F (177°C), more preferably at least about 500°F (260°C) and most preferably at least about 650°F (371°C), up to the temperature of the first reaction zone 115. In any event, vapor stream 130 is passed, without substantial cooling after separation, for blending with a second refinery stream 5 and further blending with hydrogen feed stream 140, to form a second feedstock 15 (Figs. 3, 4).

Second feedstock 15, after heating in feed furnace 10, is passed to the second reaction zone 20, which is maintained at conditions sufficient for converting at least a portion of the aromatics present in the second refinery stream, to form a second reaction zone effluent 25. The second reaction zone effluent 25 is separated in second separation zone 30 into a vapor stream 150 and a second liquid stream 35. Vapor stream 150 is purified and recycled as described for Figs. 1 and 2.

In the embodiment illustrated in Fig. 3, second liquid stream 35 is combined with first liquid stream 135, and the combined liquid stream 100 is passed to fractionation zone 40, which is typically a distillation section comprising at least one atmospheric distillation column, followed optionally by at least one vacuum distillation column. A light product, at least one middle distillate product and a liquid bottoms product are recovered. Liquid bottoms product 70 generally contains unreacted hydrocarbons from the reaction zones and hydrocarbons which boil above a target temperature, (e.g. greater than about 500°F/260°C). As shown in Fig. 3, at least a fraction of liquid bottoms 70 is recovered for further processing as recycle stream 90. Up to 100% of liquid bottoms 70 may be recycled. At least a portion of the liquid bottoms may optionally be withdrawn through product stream 75 for processing elsewhere, e.g. an FCC unit or a dewaxing unit for making a lubricating oil base stock.

In the embodiment illustrated in Fig. 4, second liquid stream 35 may contain materials which are not desirably recycled to the first reaction zone. A second refinery stream 5 containing asphaltenes, e.g. a residuum stream, is an example feedstock which results in a second liquid stream having sufficiently high amounts of asphaltenes to be detrimental to a hydrocracking catalyst contained in the first reaction zone. Accordingly, first liquid stream 135 is passed to first fraction zone 40 for separation into one or more distillate fractions and a first bottoms stream 70 and second liquid stream 35 is passed to second fractionation zone 240 for separation into one or more desulfurized distillate fractions and a second bottoms stream 270. At least a portion of first bottoms stream 70 may be recycled via first liquid recycle stream 90 to the first reaction zone, and at least a portion of second bottoms stream 270 may be recycled via second liquid recycle stream 290 to the second reaction zone.

Product streams 75 and 275 may also be recovered for use as fuels or feedstocks in other processes, including a lube process or an FCC process.

One or more distillate fractions may also be recycled to the first reaction zone for hydroprocessing under conversion conditions via third recycle stream 280, including one or more of desulfurized vacuum gas oil 260, at least a portion of desulfurized diesel stream 255 and at least a portion of desulfurized naphtha stream 250. Desulfurized C4- fraction 245 is also recovered from second fractionation zone 240.

The drawings in Figs. 1, 2, 3 and 4 show two reaction zones contained in one or two reactor vessels. It will be recognized that one or more additional reaction zones upstream of the first reaction zone, and one or more additional reaction zones downstream of the second reaction zone, may also be present in the reactor vessel or in accompanying reactor vessels. As used herein, the relative positions "upstream" and "downstream" are related to a reference position by the direction of liquid flow through the reactor vessel. Employing a minimum number of reactor vessels in the present process may be preferred for economic reasons. However, depending on the particular application of the present process, the required total catalyst volume may require multiple reaction vessels. It will be further recognized that the process as described herein may be incorporated into a larger process involving other hydroconversion reactions.

Reference is now made to the following examples of a specific embodiment of the invention, which illustrate the benefit of the process of this invention.

Example 1

A reactor system was prepared containing 65 vol% Catalyst I over 36 vol% Catalyst II (see Table I). A heavy VGO (Feed A in Table II) was contacted with 5000 SCF/Bbl hydrogen over Catalyst I. A light cycle oil (Feed B in Table II) at approximately the same volumetric flow rate was contacted, along with the effluent from Catalyst I over Catalyst II. Conditions and results are tabulated in Table III.

Table I		
	<u>Composition</u>	<u>Vol % in reactor</u>
Catalyst I	4% Ni / 20% W / 20 % USY	64
Catalyst II	3% Ni / 21% Mo / 3% P	36

Table II			
	Heavy VGO (Feed A)	Light Cycle Oil (Feed B)	Mixed Feed (Feed C): 51.5 wt % Feed A + 48.5 wt% Feed B
API Gravity	21.3	16.3	19.1
Nitrogen, ppm	716	1014	909
Sulfur, Wt %	2.93	0.59	1.72
Composition			
Paraffins	19.0		12.6
Naphthenes	25.4		21.2
Paraffins/Naphthenes		15.1	
Aromatics	55.6	81.4	66.2
Olefins		3.5	
Simulated Distillations (D 2887)	°F	°F	
0.5/5	536/671	224/389	261/433
10/30	710/786	437/502	472/579
50	834	562	701
70/90	878/937	626/706	808/899
95/99.5	967/1031	736/795	934/1003

Comparative Example

In a comparative example, the quantities of Feed A and Feed B from the examples above were combined in a mixture, and the mixture contacted with 5000 SCFB hydrogen over Catalyst A at the rate of addition used in Example 1. Effluent from Catalyst A were then introduced to Catalyst B. Conditions and results are tabulated in Table III.

As shown by the data, the cracking activity, as measured by the conversion of 680°F+ components in the feed to 680°F- components in the product, was surprisingly higher in the process of the invention than in the conventional comparative case. Even more surprising is the significantly reduced hydrogen consumption in the process of the invention, and the increased middle distillate selectivity, where middle distillate selectivity is the volumetric ratio of products boiling in the 338°-680°F range to the products boiling in the 149°-338°F range.

Reactor 1			Reactor 2						
Feed	Temp, °F	Pressure	Feed	Temp, °F	Pressure	Conversion <680°F	Hydrogen consumption, SCF/Bbl	Middle Distillate Selectivity	
Feed A	745	2300	Effluent from Reactor 1 + Feed B	675	2300	78	1440	5.7	
Feed A	745	2300		660	2300	78	1337	5.2	
Feed A	745	2300		710	2300	79	1624	4.8	
Feed C	745	2300	Effluent from Reactor 1	710	2300	63			
Feed C	755	2300		720	2300	67			
Feed C	775	2300		740	2300	75	1943	3.8	

Example II

A blended Arabian vacuum residuum feed (see Table I) was hydrotreated in a vacuum residuum hydrotreating unit.

Table I	
Arabian Blend Vacuum Residuum Feed	
Degrees API	4.6
Specific Gravity, g/cc	1.04
Sulfur, Wt %	5.73
Nitrogen, Wt %	0.47
Nickel, ppmwt	46
Vanadium, ppmwt	105
Carbon Residue, Wt %	24

Product yields from the hydrotreating step are shown in Figure Table II.

Table II				
Yields and Product Properties from Residuum Hydrotreating Step				
Liquid Products	TBP Cut Points, °F	°API	LV % of VR Feed	Sulfur, Wt %
Light Naphtha	C ₅ -180	81.7	0.36	0.007
Heavy Naphtha	180-330	56.5	2.04	0.013
Diesel	330-690	31.9	13.46	0.068
Desulfurized VGO	690-1000	18.9	27.40	0.259
VGO Product	690-1000	-	-	-
Desulfurized Residuum	1000+	12.4	60.10	0.900
Fuel Oil	690+	14.4	87.51	0.705

The desulfurized vacuum gas oil product from the residuum hydrotreating step was hydrocracked to give the products shown in Table III.

Table III				
Yields and Product Properties from Hydrocracking the Desulfurized VGO Product from the Residuum Hydrotreater				
Liquid Products	TBP Cut Points, °F	°API	LV % of Desulfurized VGO Feed	Sulfur, ppmwt
Light Naphtha	C ₅ -180	80.0	8.51	<5
Heavy Naphtha	180-330	54.0	23.99	<5
Diesel	330-690	40.0	74.80	<5
Desulfurized VGO	690-1000	-	-	-
VGO Product	690-1000	32.3	5.00	50
Desulfurized Residuum	1000+	-	-	-
Fuel Oil	690+	-	-	-

In Table IV the yields and product properties for the overall integrated process are listed. The benefit of the present invention can be seen by a comparison between the columns entitled "LV% of VR Feed" in Table II and in Table IV. Table II lists data for the comparative case, with residuum hydrotreating without hydrocracking. Table IV lists data for the invention. Including hydrocracking in the integrated process resulted in significantly higher yields of naphtha and diesel, the desired products of the process, and much lower fuel oil yields.

Table IV				
Overall Yields and Product Properties from the Combined Process of this Invention				
Liquid Products	TBP Cut Points, °F	°API	LV % of VR Feed	Sulfur, Wt %
Light Naphtha	C ₅ -180	80.2	2.69	0.001
Heavy Naphtha	180-330	54.6	8.61	0.003
Diesel	330-690	36.7	33.95	0.030
Desulfurized VGO	690-1000	-	-	-
VGO Product	690-1000	32.3	1.37	0.005
Desulfurized Residuum	1000+	12.4	60.10	0.900
Fuel Oil	1000+	12.4	60.10	0.900

Table V shows that the cetane number of the diesel product was much higher for the integrated process than for the comparative process using only residuum hydrotreating.

Table V	
	Cetane Index
Residuum hydrotreating only	45+
Hydrocracking process	60+
Process of the invention	55+

Although only specific embodiments of the present invention have been described, numerous variation can be made in these embodiments without department from the sprit of the invention and all such variations that fall within the scope of the appended claims are intended to be embraced thereby.

Claims:

1. An integrated hydroconversion process comprising:
 - a) combining a first refinery stream with a first hydrogen-rich gaseous stream to form a first feedstock;
 - b) passing the first feedstock to a first reaction zone which is maintained at a reaction temperature in the range from of from 340°C. to 455°C. (644-851°F), a reaction pressure in the range of 3.5-24.2 MPa(500-3500 pounds per square inch), employing a feed rate (vol oil/vol cat h) from 0.1 to 10 hr⁻¹ and a hydrogen circulation rate ranging from 350 std liters H₂/kg oil to 1780 std liters H₂/kg oil (2,310-11,750 standard cubic feet per barrel), thereby effecting a boiling range conversion of the first refinery stream of at least 25%, to form a first reaction zone effluent comprising normally liquid phase components and normally gaseous phase components;
 - c) combining the entire first reaction zone effluent with a second refinery stream having a boiling point range below the boiling point range of the first refinery stream to form a second feedstock;
 - d) passing the second feedstock to a second reaction zone maintained at a reaction temperature in the range from of from 340°C to 455°C (644-851°F), a reaction pressure in the range of 3.5-24.2 MPa(500-3500 pounds per square inch), employing a feed rate (vol oil/vol cat h) from 0.1 to 10 hr⁻¹ and a hydrogen circulation rate ranging from 350 std liters H₂/kg oil to 1780 std liters H₂/kg oil (2,310-11,750 standard cubic feet per barrel), which are conditions sufficient for converting at least a portion of the aromatics present in the second refinery stream, to form a second reaction zone effluent;

- e) separating the second reaction zone effluent into at least one distillate fraction and a second hydrogen-rich gaseous stream; and
 - f) recycling at least a portion of the second hydrogen-rich gaseous stream to the first reaction zone.
- 2. The process according to claim 1 wherein a boiling range conversion of between 30% and 90% occurs in the first reaction zone.
 - 3. The process according to claim 1 wherein the first refinery stream has a normal boiling point range within the temperature range 262°C-593°C (500°-1100°F).
 - 4. The process according to claim 1 wherein the first refinery stream is derived from a hydrotreating process.
 - 5. The process according to claim 1 wherein the first refinery stream is a VGO.
 - 6. The process according to claim 1 wherein at least 80% by volume of the second refinery stream boils at a temperature of less than 538°C (1000°F).
 - 7. The process according to claim 6 wherein at least 50% by volume of the second refinery stream has a normal boiling point within the middle distillate range.
 - 8. The process according to claim 7 wherein at least 80% by volume of the second refinery stream boils with the temperature range of 121°C-371°C (250°-700°F).
 - 9. The process according to claim 1 wherein the second refinery stream is a synthetic cracked stock.

10. The process according to claim 1 wherein the second refinery stream is selected from the group consisting of straight run VGO, light cycle oil, heavy cycle oil and cooker gas oil.
11. The process according to claim 1 wherein the second refinery stream has an aromatics content of greater than 50%.
12. The process according to claim 11 wherein the second refinery stream has an aromatics content of greater than 70%.
13. The process according to claim 1 wherein the entire first reaction zone effluent is passed to the second reaction zone at substantially the same temperature and at substantially the same pressure as the first reaction zone.
14. The process according to claim 13 wherein the second reaction zone is maintained at a temperature and at a pressure which are substantially the same as the temperature and the pressure maintained in the first reaction zone.
15. The process according to claim 1 wherein the second reaction zone effluent is separated in a separation zone to form at least a second hydrogen-rich gaseous stream and a liquid stream.
16. The process according to claim 15 wherein the second hydrogen-rich gaseous stream is recovered from the separation zone at a temperature in the range of 38°C-149°C (100°-300°F).
17. The process according to claim 16 wherein the liquid stream is fractionated to form at least one middle distillate stream and a bottoms product.
18. The process according to claim 17 for producing at least one middle distillate stream having a boiling range within the temperature range 121°C-371°C (250°-700°F).

19. The process according to claim 1 for producing a diesel fuel.
20. The process according to claim 1 for producing a jet fuel.
21. The process according to claim 1 wherein the distillate fraction recovered from the hydrotreater reaction zone effluent further comprises components boiling in the range C₅ –204°C (400°F).