

USE OF SUPERCRITICAL FLUID IN HYDROPROCESSING HEAVY HYDROCARBONS

FIELD OF THE INVENTION

[0001] This invention is directed to a process for producing a hydroprocessed product from residua or heavy hydrocarbon feeds. More specifically, this invention is directed to a process for producing a hydroprocessed product from a heavy hydrocarbon oil, using a supercritical fluid or solvent.

BACKGROUND

[0002] Crude oil is typically distilled to produce a variety of components that can be used directly as fuels or that are used as feedstocks for further processing or upgrading. In what is known as atmospheric distillation, a heavy residuum is produced typically that has an initial boiling point of about 650°F (343°C). This residuum is typically referred to as atmospheric residuum or as an atmospheric residuum fraction.

[0003] Atmospheric residuum fractions tend to collect a relatively high quantity of various metals, sulfur components and nitrogen components relative to the lighter distillation fractions as a result of the distillation process. Because these metal, sulfur and nitrogen components are relatively undesirable in various fuels, they are typically removed by various catalytic hydroprocessing techniques.

[0004] In some instances, the atmospheric residuum is further distilled under vacuum, i.e., at a pressure below atmospheric pressure, to recover additional distillation fractions. At vacuum conditions, additional lighter fractions can be recovered without adding to various problems encountered in atmospheric

distillation such as coking of the heavy fraction components. The heavy residuum recovered in vacuum distillation of the atmospheric residuum is typically referred to as vacuum residuum or a vacuum residuum fraction, and typically has an initial boiling point of about 1050°F (566°C). This vacuum residuum is generally higher in metals, sulfur components and nitrogen components than atmospheric residuum, and as was the case with atmospheric residuum, removal of these components is typically carried out by catalytic hydroprocessing.

[0005] Catalytic hydroprocessing of atmospheric and vacuum residua, including other heavy oils such as bitumen from oil sand, is carried out in the presence of hydrogen, using a hydroprocessing catalyst. In some processes, hydroprocessing of heavy oil or residua is carried out by adding a diluent or solvent.

[0006] Hydroprocessing of residua or other heavy oil can also include a cracking activity in which the heavy carbon components are “cracked” into smaller or lower molecular weight components. This is typically referred to as upgrading, with the upgraded product including higher volumes of fuel components.

[0007] As an example of one type of hydroprocessing process, U.S. Patent No. 3,617,525 discloses a process for removing sulfur from a hydrocarbon fraction having a boiling point above about 650°F (343°C). In carrying out the process, the hydrocarbon fraction is separated into a gas oil fraction having a boiling point between about 650°F (343°C) and about 1050°F (566°C), and a heavy residuum fraction boiling above about 1050°F (566°C). The gas oil fraction is catalytically hydrodesulfurized until the gas oil fraction contains less than 1 percent sulfur. The hydrodesulfurized gas oil is then used to dilute the heavy residuum fraction, and the diluted heavy residuum fraction is catalytically

hydrodesulfurized, producing fuels or fuel blending components reduced in sulfur content. The process is considered to provide an increased catalyst life and to use a smaller reactor volume compared to typical processes.

[0008] U.S. Patent No. 4,302,323 discloses a process for upgrading a residual petroleum fraction in which the residual fraction is mixed with a light cycle oil and hydrogen and the mixture sent through a catalytic hydrotreating zone containing a hydrotreating catalyst and then a hydrocracking zone containing a hydrocracking catalyst. Upgraded products are then separated from the effluent of the hydrocracking zone. The light cycle oil boils in the range of from 400°F (204°C) to 700°F (371°C), has a high aromatic content, and is high in nitrogen. It is considered that the light cycle oil acts more as a diluent rather than as a hydrogen donor and that the addition of the light cycle oil resulted in a substantial increase in the yield of premium products such as distillate fuels.

[0009] U.S. Patent No. 4,421,633 discloses a combination hydrodesulfurization and hydrocracking process. The feedstock can be atmospheric residuum or vacuum residuum, which is mixed with a solvent that is a recycled distillate boiling at about 400°F-700°F (204°C-371°C), considered to be equivalent to a FCC light cycle oil. The process uses a mixture of large pore and small pore catalysts such as large and small pore sulfided Ni-W catalysts. The process converts the higher boiling point residua to lower boiling point hydrocarbons by forming distillate and naphtha while removing heteroatoms, metals and carbon residuals from the higher boiling point residua.

[0010] Supercritical fluids have typically been used in the hydrocarbon processing industries to provide enhanced solubilization or extracting power for many complex organic molecules. A fluid at both a temperature and pressure that exceeds its critical temperature and pressure is considered a supercritical fluid. A supercritical fluid exists in a form in which its liquid and gaseous states

are indistinguishable from one another. The critical temperature of a fluid is the temperature above which the fluid cannot be liquefied by an increase in pressure. The critical pressure of a fluid is the vapor pressure of the fluid at its critical temperature. It has been shown that not only does the solubility of heavy materials in the supercritical fluid increase generally with temperature, but also that above the critical temperature the solubility increases with pressure, often by an order of magnitude.

[0011] Additional uses of supercritical fluids are described in U.S. Patent No. 4,483,761, which discloses the use of supercritical fluids as a cracking medium for heavy hydrocarbon oils. According to the disclosed process, heavy hydrocarbons are upgraded and cracked by contacting the heavy hydrocarbons with olefins containing five or less carbon atoms (C_5) and a solvent, at a temperature both sufficient for cracking and greater than or equal to the critical temperature of the solvent.

[0012] The ability to solubilize heavy hydrocarbons has also led to investigation of the use of supercritical conditions for hydrodenitrogenation and hydrodesulphurization of topped petroleum crudes, shale oils, etc., over conventional hydrotreating catalysts. For example, U.S. Patent No. 5,496,464 discloses a process for hydrotreating a heavy hydrocarbon oil containing a substantial portion of material that boils above 524°C to form lower boiling materials. The process comprises adding to the heavy hydrocarbon oil as solvent a paraffinic, isoparaffinic or cyclic paraffinic hydrocarbon that is hydrogen-rich and has a critical temperature of less than 500°C . The addition of the solvent to the heavy hydrocarbon oil forms a diluted feedstock mixture and the feedstock mixture is hydrotreated in the presence of activated carbon catalyst at a temperature and pressure substantially at or greater than the critical temperature and pressure of the solvent. The supercritical solvent is considered to act as a hydrogen-rich diluent to decrease the probability of recombination and

condensation of asphaltene molecules, and to enhance the degree of breakup of coke precursor “micelles,” and to enhance diffusivity of the reactant molecules into and out of the pores of the activated carbon catalyst. The solvent in conjunction with the activated carbon act in a unique way to transfer gaseous hydrogen to the heavy hydrogen-deficient feedstock.

[0013] There is a need to further develop processes for hydroprocessing heavy hydrocarbon oils to produce fuel grade products. It would be particularly desirable to hydroprocess heavy feeds that boil at or above 1050°F (566°C) (also referred to as a “1050°F+ (566°C+) fraction” herein) into molecules boiling below 1050°F (566°C) (also referred to as a “1050°F⁻ (566°C⁻) fraction” herein), while minimizing the formation of “C₄⁻” hydrocarbon compounds (i.e., hydrocarbon compounds having four carbons or less), and coke byproducts.

SUMMARY OF THE PREFERRED EMBODIMENTS OF THE INVENTION

[0014] This invention provides a process for producing hydroprocessed product. The hydroprocessed products are lighter hydrocarbon oils, which can be used to produce fuel grade products. The process provides an advantage of having a long catalyst run length.

[0015] According to one aspect of the invention, there is provided a process for producing a hydroprocessed product. The process includes a step of sending to a hydroprocessing zone (preferably located in a reactor vessel) a combined feed comprised of a heavy hydrocarbon oil component, wherein the heavy hydrocarbon oil component has a ASTM D86 10% distillation point of at least 650°F (343°C), and a solvent component in which a majority of the solvent component is comprised of at least one supercritical hydrocarbon compound having a critical temperature and pressure. The combined feed is contacted with a hydroprocessing catalyst in the hydroprocessing zone in the presence of

hydrogen at a temperature and pressure above the critical temperature and pressure of the at least one supercritical hydrocarbon compound to form the hydroprocessed product.

[0016] In a particular embodiment, the heavy hydrocarbon oil component has an initial ASTM D86 boiling point of 650°F (343°C) or greater. The heavy hydrocarbon oil can contain at least 0.0001 grams of Ni/V/Fe, on a total elemental basis of nickel, vanadium and iron.

[0017] In one embodiment, the combined feed is comprised of from 30 wt% to 90 wt% of the heavy hydrocarbon oil component and from 10 wt% to 70 wt% of the solvent component, based on total weight of the combined feed.

[0018] In another specified embodiment, the contacting of the combined feed with a hydroprocessing catalyst in the presence of hydrogen is carried out at a hydrogen partial pressure from 550 psig (3792 kPa-g) to 3000 psig (20684 kPa-g).

[0019] In yet another embodiment, the solvent component is comprised of more than one supercritical hydrocarbon compound and contacting of the combined feed with the hydroprocessing catalyst in the presence of hydrogen is carried out at a total pressure that is higher than the critical pressure of the highest-boiling point supercritical hydrocarbon compound in the solvent component.

[0020] In still another, the solvent component is comprised of more than one supercritical hydrocarbon compound and contacting of the supercritical hydrocarbon compound with the combined feed and the hydroprocessing catalyst in the presence of hydrogen is carried out at a temperature that is higher than the critical temperature of the highest-boiling point supercritical hydrocarbon compound in the solvent component.

[0021] In an alternative embodiment, the contacting is carried out at a total pressure and at a temperature at which the combined feed and the hydroprocessed products are comprised of no more than one vapor and one liquid phase during contact.

[0022] In a specific embodiment, the solvent component is comprised of at least one supercritical solvent compound selected from the group consisting of benzene, toluene, xylene, ethyl benzene, iso-propyl benzene, trimethylbenzene and tetramethylbenzene. The solvent component can be comprised of a mixture of aromatic molecules having boiling points of from 200°F (93°C) to 750°F (399°C). Alternatively, the solvent component can be comprised of a mixture of aromatic and hydroaromatic molecules having boiling points of from 200°F (93°C) to 750°F (399°C).

[0023] In another embodiment, the solvent component has an ASTM D86 10% distillation point of at least 250°F (120°C). The solvent component can be a petroleum fraction with an API gravity of at most 35°.

[0024] Preferably, the contacting is carried out at a temperature of from 320°F (160°C) to 900°F (482°C). The contacting can also be carried out at a pressure of from 600 psig (4137 kPa-g) to 3000 psig (20684 kPa-g).

[0025] In a particular embodiment, the solvent component is comprised of trimethylbenzene. For example, the solvent component is comprised of at least 50 wt % trimethylbenzene, based on total weight of the solvent component.

[0026] Preferably, the heavy hydrocarbon oil component and the solvent component are combined prior to entering the hydroprocessing zone although in embodiments of the invention, the heavy hydrocarbon oil component and the solvent component may be combined in the hydroprocessing zone. In a particular version of this embodiment, at least a portion of the solvent

component can be injected separately into an intermediate section of the hydroprocessing zone as an interbed quench. In another embodiment, the hydroprocessing zone contains the catalyst in a fixed bed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The attached Figures represent alternative embodiments of the overall invention, as well as comparative examples. The Figures pertaining to the invention are intended to be viewed as exemplary embodiments within the scope of the overall invention as claimed.

[0028] FIGURE 1 shows a comparative example of hydroprocessing of 100% Basrah resid.

[0029] FIGURE 2 shows a specific example of the invention regarding hydroprocessing of 60/40 resid/trimethylbenzene feed.

[0030] FIGURE 3 shows a comparative example of hydroprocessing of 60/40 resid/methylnaphthalene feed.

DETAILED DESCRIPTION

Introduction

[0031] This invention provides a process for producing a hydroprocessed product. The process is capable of treating residua or heavy hydrocarbon oils to produce a hydroprocessed oil product that has reduced sulfur, nitrogen, metals and "1050°F+ (566°C+) fraction" components (i.e., components that boil at 1050°F (566°C) and above) relative to the heavy oil.

[0032] The invention is particularly advantageous in that substantially longer run length can be achieved relative to conventional hydroprocessing methods. This benefit can be enhanced by operating at desired temperature and pressure using a particular solvent as a co-feed component. In particular, a majority of the solvent component is comprised of supercritical hydrocarbon compounds in which the supercritical hydrocarbon compounds have a critical temperature and pressure. The heavy hydrocarbon oil feed material and solvent co-feed are hydroprocessed by contacting the combined feed with hydroprocessing catalyst in the presence of hydrogen at a temperature and pressure above the critical temperature and pressure of the supercritical hydrocarbon compounds to form a hydroprocessed product. The hydroprocessed product has reduced sulfur, nitrogen, metals and 1050°F+ (566°C+) fraction components (i.e., components that boil at 1050°F (566°C) and above) relative to the heavy hydrocarbon oil feed component.

Heavy Hydrocarbon Oil

[0033] The hydroprocessed product is produced from a heavy hydrocarbon oil component. Examples of heavy hydrocarbon oils include, but are not limited to, heavy crude oils, distillation residues, heavy oils coming from catalytic treatment (such as fluid catalytic cracking), tars (such as oils from visbreaking or similar thermal processes), oils (such as bitumen) from oil sands and heavy oils derived from coal.

[0034] Heavy hydrocarbon oils can be liquid, semi-solid, and/or solid at atmospheric conditions. Additional examples of heavy oils that can be hydroprocessed, treated or upgraded according to this invention include Athabasca bitumen, vacuum resid from Brazilian Santos and Campos basins, Egyptian Gulf of Suez, Chad, Venezuelan Zulia, Malaysia, and Indonesia Sumatra. Other examples of heavy hydrocarbon oil include residuum from

refinery distillation processes, including atmospheric and vacuum distillation processes. Such heavy hydrocarbon oils can have an initial ASTM D86 boiling point of 650°F (343°C) or greater. Preferably, the heavy hydrocarbon oil will have an ASTM D86 10% distillation point of at least 650°F (343°C), alternatively at least 660°F (349°C), or at least 750°F (399°C), or at least 1020°F (549°C).

[0035] Heavy hydrocarbon oils can be relatively high in total acid number (TAN). For example, heavy hydrocarbon oils that can be hydroprocessed according to this invention have a TAN of at least 0.1, at least 0.3, or at least 1.

[0036] The density, or weight per volume, of the heavy hydrocarbon can be determined according to ASTM D287-92(2006) Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method), and is provided in terms of API gravity. In general, the higher the API gravity, the less dense the oil. API gravity is at most 20° in one embodiment, at most 15° in another embodiment, and at most 10° in another embodiment.

[0037] Heavy hydrocarbon oils can be high in metals. For example, the heavy hydrocarbon oil can be high in total nickel, vanadium and iron contents. In one embodiment, the heavy hydrocarbon oil will contain at least 0.00005 grams of Ni/V/Fe (50 ppm) or at least 0.0002 grams of Ni/V/Fe (200 ppm) per gram of heavy hydrocarbon oil, on a total elemental basis of nickel, vanadium and iron.

[0038] Contaminants such as nitrogen and sulfur are found in heavy hydrocarbon oils, often in organically-bound form. Nitrogen content can range from about 50 wppm to about 5000 wppm elemental nitrogen, or about 75 wppm to about 800 wppm elemental nitrogen, or about 100 wppm to about 700 wppm, based on total weight of the heavy hydrocarbon component. The nitrogen

containing compounds can be present as basic or non-basic nitrogen species. Examples of basic nitrogen species include quinolines and substituted quinolines. Examples of non-basic nitrogen species include carbazoles and substituted carbazoles.

[0039] Sulfur content of heavy hydrocarbon oils generally ranges from about 500 wppm to about 100,000 wppm elemental sulfur, or from about 1000 wppm to about 50,000 wppm, or from about 1000 wppm to about 30,000 wppm, based on total weight of the heavy hydrocarbon component. Sulfur will usually be present as organically bound sulfur. Examples of such sulfur compounds include the class of heterocyclic sulfur compounds such as thiophenes, tetrahydrothiophenes, benzothiophenes and their higher homologs and analogs. Other organically bound sulfur compounds include aliphatic, naphthenic, and aromatic mercaptans, sulfides, di- and polysulfides.

[0040] Heavy hydrocarbon oils can be high in n-pentane asphaltenes. In one embodiment, the heavy hydrocarbon oil will contain at 5 wt% or at least 15 wt% n-pentane asphaltenes.

Solvent

[0041] The solvent component that is used according to this invention is comprised of at least one supercritical solvent compound, in which a supercritical solvent compound is defined as a compound, i.e., hydrocarbon compound, having a critical point, such as a critical temperature and critical pressure. A hydrocarbon compound is defined as a compound having at least one hydrogen atom and at least one carbon atom. A critical point is the temperature and pressure at which a phase boundary of the hydrocarbon ceases to exist. A preferred supercritical solvent compound of this invention is a hydrocarbon oil solvent that has a vapor-liquid critical point below the operating

temperature and pressure at which the hydroprocessing process is being carried out.

[0042] According to this invention, the solvent component can include supercritical solvent compounds as well as hydrocarbons that are not considered supercritical solvent compounds. Preferably, a majority (i.e., at least 50 wt % based on total solvent weight) of the solvent component is comprised of one or more supercritical compounds. Alternatively, the solvent can be comprised of at least 60 wt% or 70 wt% or 80 wt% or 90 wt%, based on total solvent weight, of supercritical compounds.

[0043] The supercritical solvent compounds contained in the solvent composition preferably have a critical temperature of at least 300°F (149°C). The compounds can be hydrocarbons or organic derivatives of hydrocarbons and other organic compounds that have a critical temperature of at least 300°F (149°C). Preferably, these compounds have a critical temperature of not greater than 840°F (449°C). In a particular embodiment, the supercritical compounds have a critical temperature of at least 350°F (177°C), or at least 480°F (249°C), or at least 600°F (316°C), and not greater than 750°F (399°C).

[0044] The supercritical solvent compounds contained in the solvent component preferably have a critical pressure of not greater than 500 psig (3447 kPa-g). More preferably, the supercritical solvent compounds contained in the solvent component have a critical pressure of not greater than 400 psig (2750 kPa-g), alternatively 350 psig (2413 kPa-g), alternatively not greater than 300 psig (2068 kPa-g), or alternatively not greater than 250 psig (1724 kPa-g). Preferably, the supercritical solvent compounds contained in the solvent component have a critical pressure of at least 50 psig (345 kPa-g), or at least 100 psi (389 kPa-g), or at least 150 psig (1034 kPa-g).

[0045] The supercritical solvent compounds contained in the solvent composition have boiling points of not greater than 750°F (399°C). In a preferred embodiment, none of the supercritical solvent compounds contained in the solvent composition has a boiling point of greater than 600°F (316°C), or greater than 550°F (288°C), or greater than 500°F (260°C), or greater than 450°F (232°C), or greater than 400°F (204°C).

[0046] At the hydroprocessing temperature, i.e., the temperature in the contacting zone in which the combined heavy hydrocarbon oil and the solvent co-feed contact the hydroprocessing catalyst, the supercritical solvent compounds will be in a supercritical or near-supercritical state. Under hydroprocessing conditions, the solvent components should be much less reactive than residual oils. Preferably, the supercritical compounds undergo no greater than 30 percent decomposition, particularly no greater than 20 percent decomposition, during hydroprocessing.

[0047] Suitable supercritical compounds that can be used as the solvent of this invention include aromatic hydrocarbons having one, two or three rings, hydroaromatic compounds, alicyclic compounds and aliphatic compounds or mixtures thereof. For example, the solvent component can be comprised of a mixture of aromatic molecules having boiling points of from 200°F (93°C) to 750°F (399°C), or from 240°F (116°C) to 710°F (377°C), or from 260°F (127°C) to 660°F (349°C).

[0048] Another example of aromatic hydrocarbon includes aromatic hydrocarbons having a single benzene ring and preferably not more than 4 carbon atoms in substituent groups. Examples of such compounds include, but are not limited to, benzene, toluene, xylene, ethyl benzene, iso-propyl benzene, trimethylbenzene, and tetramethylbenzene. Thus, a solvent feedstream containing at least a majority of one or more of these compounds can be used in

the hydroprocessing at the predetermined hydroprocessing temperatures further described below.

[0049] Aromatic hydrocarbons having two aromatic rings can also be used as supercritical solvent compounds. Since these compounds tend to have higher critical temperatures, hydroprocessing can be carried out at higher temperatures such as at the predetermined temperatures further described below. Examples of these compounds include, but are not limited to naphthalene, methyl naphthalene, biphenyl and biphenyl methane.

[0050] According to another embodiment of the invention, the solvent component can be comprised of a mixture of aromatic and hydroaromatic molecules. For example, the solvent component can be comprised of a mixture of aromatic and hydroaromatic molecules having boiling points of from 200°F (93°C) to 750°F (399°C), or from 250°F (121°C) to 660°F (349°C), or from 300°F (149°C) to 600°F (316°C).

[0051] Hydroaromatic compounds having at least two rings, including those having hydrocarbon substituents, are representative of preferred supercritical solvent compounds. In particular, the preferred hydroaromatic compounds are two ring hydrocarbon compounds in which one ring is saturated and one is unsaturated. Examples of these compounds include, but are not limited to, tetralin and methyl tetralin.

[0052] Alicyclic hydrocarbons, particularly unsaturated alicyclic hydrocarbons, can also be employed as supercritical solvent compounds. Examples of such compounds include, but are not limited to, alicyclic hydrocarbons having at least five carbon atoms such as cyclopentane, cyclohexane, cis- and transdecalin and alkylated derivatives thereof. In one embodiment, the alicyclic hydrocarbons have no more than 12 carbon atoms.

Additional examples include naphthenic-containing fractions of kerosene such as those fractions having an initial and final boiling points in the range of 200°F (93°C) to 750°F (399°C) and a naphthenic concentration of at least 10 wt % or at least 15 wt%, based on the total weight of the solvent feedstream.

[0053] Aliphatic hydrocarbons having at least five carbon atoms, but not more than 16 carbon atoms can also be employed. Examples of such hydrocarbons include, but are not limited to, pentanes, hexanes, octanes, dodecanes and hexadecanes.

[0054] In one embodiment, the solvent component has an ASTM D86 10% distillation point of at least 250°F (120°C). Alternatively, the solvent component has an ASTM D86 10% distillation point of at least 275°F (135°C) or at least 300°F (149°C).

[0055] The solvent component preferably has an ASTM D86 90% distillation point of not greater than 575°F (302°C). Alternatively, the solvent component has an ASTM D86 90% distillation point of not greater than 550°F (288°C) or not greater than 500°F (260°C), or not greater than 450°F (232°C), or not greater than 400°F (204°C).

[0056] The density of the solvent component can also be determined according to ASTM D287-92(2006) Standard Test Method for API Gravity of Crude Petroleum and Petroleum Products (Hydrometer Method) in terms of API gravity. API gravity of the solvent component is at most 35° in one embodiment, at most 30° in another embodiment, and at most 25° in another embodiment.

[0057] The solvent component should be combined with the heavy hydrocarbon oil component to produce a combined feedstock for the contacting zone of a hydroprocessing reactor. For example, such a feedstock is comprised

of from 30 wt% to 95 wt% of the heavy hydrocarbon oil component and from 5 wt% to 70 wt% of the solvent component, based on the total weight of the combined feed. Alternatively, the combined feedstock is comprised of from 40 wt% to 80 wt% of the heavy hydrocarbon oil component and from 10 wt% to 60 wt% of the solvent component, based on total weight of the combined feed.

[0058] The solvent can be combined with the heavy hydrocarbon oil within the hydroprocessing vessel or hydroprocessing zone. Alternatively, the solvent and heavy hydrocarbon oil can be supplied as separate streams and combined into one feed stream prior to entering the hydroprocessing vessel or hydroprocessing zone.

Hydroprocessing Catalysts

[0059] Suitable hydroprocessing catalysts for use in the present invention can include conventional hydroprocessing catalysts and particularly those that comprise at least one Group VIII non-noble metal, preferably Fe, Co, and/or Ni, such as Co and/or Ni; and at least one Group VI metal, preferably Mo and/or W. Such hydroprocessing catalysts optionally include transition metal sulfides that are impregnated or dispersed on a refractory support or carrier such as alumina and/or silica. The support or carrier itself typically has no significant/measurable catalytic activity. Substantially carrier- or support-free catalysts, commonly referred to as bulk catalysts, generally have higher volumetric activities than their supported counterparts.

[0060] The catalysts used in the present invention can either be in bulk form or in supported form. In addition to alumina and/or silica, other suitable support/carrier materials can include, but are not limited to, zeolites, titania, silica-titania, and titania-alumina. It is within the scope of the present invention

that more than one type of hydroprocessing catalyst can be used in one or multiple reaction vessels.

[0061] The at least one Group VIII non-noble metal, in oxide form, can typically be present in an amount ranging from about 2 wt% to about 30 wt%, preferably from about 4 wt% to about 15 wt%. The at least one Group VI metal, in oxide form, can typically be present in an amount ranging from about 2 wt% to about 60 wt%, preferably from about 6 wt% to about 40 wt% or from about 10 wt% to about 30 wt%. These weight percents are based on the total weight of the catalyst.

[0062] A vessel or hydroprocessing zone in which catalytic activity occurs can include one or more hydroprocessing catalysts. Such catalysts can be mixed or stacked, with the catalyst preferably being in a fixed bed in the vessel or hydroprocessing zone.

[0063] The support can be impregnated with the desired metals to form the hydroprocessing catalyst. In particular impregnation embodiments, the support is heat treated at temperatures in a range of from 400°C to 1200°C, or from 450°C to 1000°C, or from 600°C to 900°C, prior to impregnation with the metals.

[0064] In an alternative embodiment, the hydroprocessing catalyst is comprised of shaped extrudates. The extrudate diameters range from 1/32nd to 1/8th inch, from 1/20th to 1/10th inch, or from 1/20th to 1/16th inch. The extrudates can be cylindrical or shaped. Non-limiting examples of extrudate shapes include trilobes and quadralobes.

[0065] The process of this invention can be effectively carried out using a hydroprocessing catalyst having any median pore diameter effective for hydroprocessing the heavy oil component. For example, the median pore

diameter can be in a range of from 30 to 1000 Å (Angstroms), or 50 to 500 Å, or 60 to 300 Å. Pore diameter is preferably determined according to ASTM Method D4284-07 Mercury Porosimetry.

[0066] In a particular embodiment, the hydroprocessing catalyst has a median pore diameter in a range of from 50 to 200 Å. Alternatively, the hydroprocessing catalyst has a median pore diameter in a range of from 90 to 180 Å, or 100 to 140 Å, or 110 to 130 Å.

[0067] In another embodiment, the hydroprocessing catalyst has a median pore diameter ranging from 50 Å to 150 Å. Alternatively, the hydroprocessing catalyst has a median pore diameter in a range of from 60 Å to 135 Å, or from 70 Å to 120 Å.

[0068] The process of this invention is also effective with hydroprocessing catalysts having a larger median pore diameter. For example, the process can be effective using a hydroprocessing catalyst having a median pore diameter in a range of from 180 to 500 Å, or 200 to 300 Å, or 230 to 250 Å.

[0069] It is preferred that the hydroprocessing catalyst have a pore size distribution that is not so great as to negatively impact catalyst activity or selectivity. For example, the hydroprocessing catalyst can have a pore size distribution in which at least 60% of the pores have a pore diameter within 45 Å, 35 Å, or 25 Å of the median pore diameter. In certain embodiments, the catalyst has a median pore diameter in a range of from 50 to 180 Å, or from 60 to 150 Å, with at least 60% of the pores having a pore diameter within 45 Å, 35 Å, or 25 Å of the median pore diameter.

[0070] Pore volume should be sufficiently large to further contribute to catalyst activity or selectivity. For example, the hydroprocessing catalyst can have a pore volume of at least 0.3 cm³/g, at least 0.7 cm³/g, or at least 0.9 cm³/g.

In certain embodiments, pore volume can range from 0.3-0.99 cm³/g, 0.4-0.8 cm³/g, or 0.5-0.7 cm³/g.

[0071] In certain embodiments, the catalyst exists in shaped forms, for example, pellets, cylinders, and/or extrudates. The catalyst typically has a flat plate crush strength in a range of from 50-500 N/cm, or 60-400 N/cm, or 100-350 N/cm, or 200-300 N/cm, or 220-280 N/cm.

Hydrogen Stream

[0072] Hydroprocessing is carried out in the presence of hydrogen. A hydrogen stream is, therefore, fed or injected into a vessel or reaction zone (or “hydroprocessing zone”) in which the hydroprocessing catalyst is located. Hydrogen, which is contained in a hydrogen “treat gas,” is provided to the reaction zone. Treat gas, as referred to in this invention, can be either pure hydrogen or a hydrogen-containing gas, which is a gas stream containing hydrogen in an amount that is sufficient for the intended reaction(s), optionally including one or more other gases (e.g., nitrogen and light hydrocarbons such as methane), and which will not adversely interfere with or affect either the reactions or the products. Impurities, such as H₂S and NH₃ are undesirable and would typically be removed from the treat gas before it is conducted to the reactor. The treat gas stream introduced into a reaction stage will preferably contain at least about 50 vol. % and more preferably at least about 75 vol. % hydrogen.

[0073] Hydrogen-containing treat gas can be supplied at a rate of from 300 SCF/B (standard cubic feet of hydrogen per barrel of feed) (53 S m³/m³) to 5000 SCF/B (891 S m³/m³). Preferably, the treat gas is provided in a range of from 1000 SCF/B (178 S m³/m³) to 3000 SCF/B (534 S m³/m³).

[0074] Hydrogen-containing treat gas can be supplied co-currently with the heavy hydrocarbon oil and/or solvent or separately via a separate gas conduit to the hydroprocessing zone. The contact of the heavy hydrocarbon oil and solvent with the hydroprocessing catalyst and the hydrogen treat gas produces a total product that includes a hydroprocessed oil product, and, in some embodiments, gas.

Processing Conditions

[0075] Hydroprocessing (alternatively hydroconversion) generally refers to treating or upgrading the heavy hydrocarbon oil component that contacts the hydroprocessing catalyst. Hydroprocessing particularly refers to any process that is carried out in the presence of hydrogen, including, but not limited to, hydroconversion, hydrocracking, hydrogenation, hydrotreating, hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, hydrodearomatization, hydroisomerization, and hydrodewaxing including selective hydrocracking. The hydroprocessing reaction is carried out in a vessel or a hydroprocessing zone in which heavy hydrocarbon and solvent contact the hydroprocessing catalyst in the presence of hydrogen.

[0076] Contacting conditions in the hydroprocessing zone can include, but are not limited to, temperature, pressure, hydrogen flow, hydrocarbon feed flow, or combinations thereof. Contacting conditions in some embodiments are controlled to yield a product with specific properties.

[0077] Temperature in the contacting zone is higher than the critical temperature of the supercritical solvent compound in the solvent component that has the highest critical temperature of all supercritical solvent compounds present in the solvent component. For example, the temperature in the contacting zone is at least 10°C, or at least 30°C, or at least 50°C higher than the

critical temperature of the supercritical solvent compound in the solvent component that has the highest critical temperature of all supercritical solvent compounds present in the solvent component. As a further example, the temperature in the contacting zone can range from 320°F (160°C) to 900°F (482°C), or from 350°F (177°C) to 800°F (427°C), or from 500°F (260°C) to 700°F (371°C), or from 550°F (288°C) to 650°F (343°C). In some embodiments, temperature in the contacting zone can range from 560°F (293°C) to 850°F (454°C), or 660°F (349°C) to 790°F (421°C), or 680°F (360°C) to 750°F (399°C).

[0078] Total pressure in the contacting zone is higher than the critical pressure of the supercritical solvent compound in the solvent component that has the highest critical pressure of all supercritical solvent compounds present in the solvent component. For example, the total pressure in the contacting zone is at least 10 psig (69 kPa-g), or at least 20 psig (138 kPa-g), or at least 30 psig (207 kPa-g) higher than the critical pressure of the supercritical solvent compound in the solvent component that has the highest critical pressure of all supercritical solvent compounds present in the solvent component. As a further example, the total pressure in the contacting zone can range from 600 psig (4137 kPa-g) to 3000 psig (20684 kPa-g), more preferably from 650 psig (4482 kPa-g) to 2000 psig (13790 kPa-g), and most preferably from 800 psig (5516 kPa-g) to 1500 psig (10342 kPa-g).

[0079] Liquid hourly space velocity (LHSV) of the combined heavy hydrocarbon oil and solvent components will generally range from 0.1 to 30 h⁻¹, or 0.4 h⁻¹ to 25 h⁻¹, or 0.5 to 20 h⁻¹. In some embodiments, LHSV is at least 15 h⁻¹, or at least 10 h⁻¹, or at least 5 h⁻¹.

[0080] Partial pressure of hydrogen in the contacting zone can range from 550 psig (3792 kPa-g) to 3000 psig (20684 kPa-g). Preferably, the contacting of

the combined feed with hydroprocessing catalyst in the presence of hydrogen is carried out at a hydrogen partial pressure of from 650 psig (4482 kPa-g) to 2000 psig (13790 kPa-g), and more preferably from 800 psig (5516 kPa-g) to 1500 psig (10342-g).

Hydroprocessed Product

[0081] Relative to the heavy hydrocarbon oil component in the feedstream, the hydroprocessed product will be a material or crude product that exhibits reductions in such properties as average molecular weight, boiling point range, density and/or concentration of sulfur, nitrogen, oxygen, and metals.

[0082] In an embodiment, contacting the heavy hydrocarbon oil and solvent with the hydroprocessing catalyst in the presence of hydrogen to produce a hydroprocessed product is carried out in a single contacting zone. In another embodiment, contacting is carried out in two or more contacting zones. The total hydroprocessed product can be separated to form one or more particularly desired liquid products and one or more gas products.

[0083] In some embodiments, the liquid product is blended with a hydrocarbon feedstock that is the same as or different from the heavy hydrocarbon oil component. For example, the liquid hydroprocessed product can be combined with a hydrocarbon oil having a different viscosity, resulting in a blended product having a viscosity that is between the viscosity of the liquid hydroprocessed product and the viscosity of the heavy hydrocarbon oil component.

[0084] In some embodiments, the hydroprocessed product and/or the blended product are transported to a refinery and distilled to produce one or more distillate fractions. The distillate fractions can be catalytically processed to

produce commercial products such as transportation fuels, lubricants, or chemicals.

[0085] In some embodiments, the hydroprocessed product has a total Ni/V/Fe content of at most 50%, or at most 10%, or at most 5%, or at most 3%, or at most 1% of the total Ni/V/Fe content of the heavy hydrocarbon oil component. In certain embodiments, the fraction of the hydroprocessed product that has a boiling point of 650°F (343°C) and higher (i.e., 650°F+ (343°C+) product fraction) has, per gram of 650°F+ (343°C+) product fraction, a total Ni/V/Fe content in a range of from 1×10^{-7} grams to 2×10^{-4} grams (0.1 to 200 ppm), or 3×10^{-7} grams to 1×10^{-4} grams (0.3 to 100 ppm), or 1×10^{-6} grams to 1×10^{-4} grams (1 to 100 ppm). In certain embodiments, the 650°F+ (343°C+) product fraction has not greater than 4×10^{-5} grams of Ni/V/Fe (40 ppm).

[0086] In certain embodiments, the hydroprocessed product has an API gravity that is 100-160%, or 110-140% of that of the heavy hydrocarbon oil component. In certain embodiments, API gravity of the hydroprocessed product is from 10°-40°, or 12°-35°, or 14°-30°.

[0087] In certain embodiments, the hydroprocessed product has a viscosity of at most 90%, or at most 80%, or at most 70% of that of the heavy hydrocarbon oil component. In some embodiments, the viscosity of the hydroprocessed product is at most 90% of the viscosity of the heavy hydrocarbon oil component, while the API gravity of the hydroprocessed product is 100-160%, or 105-155%, or 110-150% of that of the heavy hydrocarbon oil component.

[0088] In an alternative embodiment, the 650°F+ (343°C+) product fraction can have a viscosity at 100°C of 10 to 150 cst, or 15 to 120 cst, or 20-100 cst. Most atmospheric resids of crude oils range from 40 to 200 cst. In certain

embodiments, 650°F+ (343°C+) product fraction has a viscosity of at most 90%, or at most 50%, or at most 5% of that of the heavy hydrocarbon oil component.

[0089] In some embodiments, the hydroprocessed product has a total heteroatom (i.e., S/N/O) content of at most 50%, or at most 10%, or at most 5% of the total heteroatom content of the heavy hydrocarbon oil component.

[0090] In some embodiments, the sulfur content of the hydroprocessed product is at most 50%, or at most 10%, or at most 5% of the sulfur content of the heavy hydrocarbon feedstock. The total nitrogen content of the hydroprocessed product is at most 50%, or at most 10%, or at most 5% of that of the heavy hydrocarbon feedstock, and the hydroprocessed product has a total oxygen content that is at most 75%, or at most 50%, or at most 30%, or at most 10%, or at most 5% of the total oxygen content of the heavy hydrocarbon oil component.

Examples

Example 1

[0091] A fixed bed, downflow reactor was constructed from 3/8th inch stainless steel tubing. Two 50 cm brass half cylinders were bolted onto the 3/8th inch tube. The volume of the hot zone inside the brass cylinder was 16.0 cc's. The reactor was loaded with 5 cc of a supported NiMo hydroprocessing catalyst on top of 8 cc of an unsupported NiMoW hydroprocessing catalyst. The supported NiMo catalyst was used primarily for removing metals from heavy oil feedstocks. The catalyst system was sulfided using a feedstock comprised of 80 wt% 130-neutral lube oil/20 wt% ethyl-disulfide.

[0092] The feedstock was fed at 3000 SCF/B (standard cubic feet of hydrogen per barrel of feed), 644°F (340°C), 0.2 LHSV, and 1000 psig (6895

kPa-g) for 48 hours. The feedstock was then switched to 60 wt% Athabasca bitumen/40 wt% trimethylbenzene (TMB). Reaction conditions were changed to 800 psig (5516 kPa-g), 5 cc/hr liquid feed, and 1100 SCF/B hydrogen (197 S m³/m³). The reactor temperature was varied between 689°F (365°C) and 780°F (416°C).

[0093] The Athabasca bitumen had the following properties: 4.8 wt% S, 5000 ppm N, 55% 450°F (232°C) to 1050°F(566°C), 45 wt% 1050°F+ (566°C+) fraction, 0.9950 specific gravity at 60°F, 67 wppm Ni, 166 wppm V, and 13 wppm Fe.

[0094] During the run, the hydrodesulfurization and hydrodemetallization levels were typically held between 60 and 70% through temperature adjustment. The deposition of metals in the reactor was tracked with time. For example, at the time that the catalyst had accumulated 5 wt% metals, the conditions were 800 psig (5516 kPa-g) and 725°F (385°C). Less than 1 wt% of the TMB was hydrogenated and/or hydrocracked.

[0095] The catalyst was run for 150 days. Its HDS activity dropped by less than 1% over a 3-week period at a temperature as high as 780°F (416°C). The run was voluntarily terminated to enable examination of the metals distribution on the catalyst before metal loading filled any more of the catalyst void volume.

[0096] The total metal loading on the catalyst was 14 wt%. Upon ending the run, the catalysts were analyzed for vanadium profile in the extrudates. The vanadium deposit across whole extrudates was found to be evenly deposited throughout the extrudate on both catalysts, indicative of insignificant pore mouth plugging. Analysis of the spent catalysts showed that the metals uptake of both catalysts were similar— close to 0.14 g metal/cc of catalyst. This example demonstrates that upgrading of Athabasca bitumen in the presence of TMB at a

moderate pressure of 800 psig (5516 kPa-g) can be achieved for an extended period of time without reactor plugging problems. Moreover, there is little metal buildup inside catalyst pores.

[0097] Under the conditions used, TMB is a supercritical fluid. As such, it helps reduce oil viscosity and hence accelerate diffusion rate inside catalyst particles. A supercritical solvent also changes the phase behavior around the catalyst particles by reducing the tendency of forming two incompatible liquid phases during the reaction, thus mitigating the deposition and accumulation of carbonaceous species on the catalyst.

Examples 2-4

[0098] The feedstock and catalyst used in Examples 2-4 were a Basrah atmospheric resid and a supported Co-Mo catalyst. The following solvents were used: trimethylbenzene (TMB) and methylnaphthalene (MN). A base-case hydroconversion experiment was done in the absence of an added solvent.

[0099] Specifically, the following four feedstocks were used in the examples:

Ex. 2: 100% Basrah resid

Ex. 3: 60% Basrah resid and 40% TMB

Ex. 4: 60% Basrah resid and 40% MN

[00100] Table 1 shows the properties of the Basrah atmospheric resid.

Table 1

Feed Description

Feed	Basrah Atmospheric Resid
C ₅ -400°F	0
400-650°F	3
650-1050°F	55
1050°F ⁺	42
API Gravity	12.3
S, wt%	4.6
N, wt%	0.26
Ni, wppm	22
Va, wppm	79

[00101] The experiments of Examples 2-4 were carried out in an upflow fixed-bed reactor. The catalyst extrudates were crushed and screened to 40/60 mesh granules. Liquid sulfiding was carried out with ethyl disulfide dissolved in a lubricating oil at 340°C. Each experimental run was started with the standard conditions of 725°F (385°C), 750 psig (5171 kPa) H₂, 0.17 total LHSV, and 3000 SCF hydrogen/B of feed (534 S m³/m³). During the run, the loss of catalyst activity was countered by raising reactor temperature.

Example 2 (Comparative)

[00102] A base case run was conducted with neat Basrah resid (i.e., 100% resid, no solvent) as described above for this Example. Figure 1 shows the performance of the catalyst. The catalyst was on stream for 18 days with decreasing activities for 1050°F+ (566°C+) fraction conversion, HDM, HDS, and HDN. After 18 days, the run was forced to shut down due to excessive reactor pressure drop.

Example 3

[00103] A run was conducted with 60% Basrah resid and 40% trimethylbenzene (TMB) as described above for this Example. The 1050°F+ (566°C+) fraction conversion and HDN reached a relatively stable level after 18 days. While HDM and HDS both declined gradually, their levels were markedly higher than those shown in Example 2.

[00104] The reactor temperature was raised to 752°F (400°C) after 40 days and then to 797°F (425°C) after 62 days. The consequent increases in 1050°F+ (566°C+) fraction conversion, HDM, HDS, and HDM can be seen in Fig. 2. After 80 days on stream, the reactor temperature was further increased to 842°F (450°C). After 3 days at this temperature, the run was terminated due to reactor plugging.

[00105] Figure 2 also shows the catalyst performance with the 60/40 resid/TMB feed. This run was on stream for 82 days, much longer than the base case run as shown in Example 2.

[00106] The third plot in Fig. 2 further shows the quality of the liquid product is much better than that obtained from the neat resid run of Example 2. More importantly, here a far more sustainable operation can be achieved at a high 70% 1050°F+ (566°C+) fraction conversion and a relatively low hydrogen pressure of 750 psig (5171 kPa).

[00107] It should be noted that the hydrogenation of TMB under the reaction conditions is negligible.

[00108] In summary, the TMB-as-solvent experiment permits scanning a temperature range of 725°F (385°C) to 842°F (450°C), whereas the no-solvent run (Example 2) was restricted to 725°F (385°C) due to operability problem.

The results disclosed in Examples 1-3 show that the presence of a supercritical solvent significantly increases a catalyst's productivity by prolonging its run length.

Example 4 (Comparative)

[00109] This experiment was carried out using 60% Basrah resid and 40% methylnaphthalene (MN) at the same conditions as those used in Example 3 for the first 42 days. Figure 3 shows the performance data of this Example. As seen from Figure 3, the reaction temperature was increased from 725°F (385°C) to 752°F (400°C) after 42 days on stream and to 797°F (425°C) after 66 days.

[00110] The catalyst performances in terms of 1050°F+ (566°C+) fraction conversion, HDM, HDS, and HDN were inferior to those observed with the 40% TMB case. This indicates that MN solvent is less effective than TMB. Under the conditions used, MN is in a subcritical state because the reaction temperature is lower than the critical temperature.

[00111] Specifically, the performance difference between TMB and MN in terms of product quality is compared at a constant resid throughput (space time yield) of 103g resid processed per g of catalyst. As can be seen from Table 2, the 40 %TMB run gives higher 1050°F+ (566°C+) fraction conversion, HDM, HDS, and HDN. Also, the C₄⁻ (compounds having four carbons or less) yield is lower. Note also that the TMB-as-solvent experiment permits scanning a temperature range of 725°F (385°C) to 842°F, whereas the no-solvent run (Example 2) was restricted to 725°F (385°C) due to operability problem. These results show that the supercritical solvent TMB gives better results than the subcritical solvent MN.

Table 2

Performance Comparison at a Constant Resid Throughput

Feed, wt%	100% Resid	60/40 Resid/TMB	60/40 Resid/MN
Resid processed/cat, g/g (Stream time)	103 (18 days)	102 (32 days)	103 (32 days)
1050°F ⁺ Conversion, %	42	52	48
HDM, %	75	93	79
HDS, %	52	75	57
HDN, %	7	28	18
Product Distribution, wt%			
H ₂ S	2.1	3.2	2.3
C ₄ ⁻ gas	1.9	2.8	5.5
C ₅ -400°F (naphtha)	3.3	6.1	11.5
400-650°F (distillate)	11.4	15.4	8.8
650-1050°F (gas oil)	55.8	54.0	53.6
<u>1050°F[±]</u>	<u>25.5</u>	<u>18.5</u>	<u>18.4</u>
Sum	100	100	100

[00112] Instead of feeding the appropriate light aromatic solvent from the reactor inlet, part of the solvent may be fed to the reactor via interbed quench zones. This would allow the solvent to help control reaction exothermicity (adiabatic temperature rise) and improve the liquid flow distribution in the reactor bed. The use of the appropriate light aromatic solvent has the additional benefit because of relatively straightforward separation and solvent recycle.

[00113] The principles and modes of operation of this invention have been described above with reference to various exemplary and preferred embodiments. As understood by those of skill in the art, the overall invention, as defined by the claims, encompasses other preferred embodiments not specifically enumerated herein.

CLAIMS:

1. A process for producing a hydroprocessed product, comprising:

sending to a hydroprocessing zone a combined feed comprised of a heavy hydrocarbon oil component, wherein the heavy hydrocarbon oil component has a ASTM D86 10% distillation point of at least 650°F (343°C), and a solvent component in which a majority of the solvent is comprised of at least one supercritical hydrocarbon compound having a critical temperature and pressure;

and

contacting the combined feed with a hydroprocessing catalyst in the presence of hydrogen at a temperature and pressure above the critical temperature and pressure of the at least one supercritical hydrocarbon compound to form the hydroprocessed product.
2. The process of claim 1, wherein the heavy hydrocarbon oil component has an initial ASTM D86 boiling point of 650°F (343°C) or greater.
3. The process of claim 1, wherein the heavy hydrocarbon oil component contains at least 0.0001 grams of Ni/V/Fe, on a total elemental basis of nickel, vanadium and iron.
4. The process of claim 1, wherein the combined feed is comprised of from 30 wt% to 90 wt% of the heavy hydrocarbon oil component and from 10 wt% to 70 wt% of the solvent component, based on total weight of the combined feed.
5. The process of claim 1, wherein the contacting of the combined feed with the hydroprocessing catalyst in the presence of hydrogen is carried out at a hydrogen partial pressure from 550 psig (3792 kPa-g) to 3000 psig (20684 kPa-g).

6. The process of claim 1, wherein the solvent component is comprised of more than one supercritical hydrocarbon compound and contacting of the combined feed with the hydroprocessing catalyst in the presence of hydrogen is carried out at a total pressure that is higher than the critical pressure of the highest-boiling supercritical hydrocarbon compound in the solvent component.

7. The process of claim 6, wherein the solvent component is comprised of a mixture of aromatic molecules having boiling points of from 200°F (93°C) to 750°F (399°C).

8. The process of claim 4, wherein the solvent component is comprised of more than one supercritical hydrocarbon compound and contacting of the combined feed with the hydroprocessing catalyst in the presence of hydrogen is carried out at a temperature that is higher than the critical temperature of the highest-boiling supercritical hydrocarbon compound in the solvent component.

9. The process of claim 1, wherein the contacting is carried out at a total pressure and at a temperature at which the combined feed and the hydroprocessed products are comprised of no more than one vapor and one liquid phase during contact.

10. The process of claim 1, wherein the solvent component is comprised of at least one supercritical solvent compound selected from the group consisting of benzene, toluene, xylene, ethyl benzene, iso-propyl benzene, trimethylbenzene, and tetramethylbenzene.

11. The process of claim 1, wherein the solvent component is comprised of a mixture of aromatic and hydroaromatic molecules having boiling points of from 200°F (93°C) to 750°F (399°C).

12. The process of claim 1, wherein the solvent component has an ASTM D86 10% distillation point of at least 250°F (120°C).

13. The process of claim 1, wherein the solvent component is a petroleum fraction with an API gravity of less than or equal to 35°.

14. The process of claim 1, wherein the contacting is carried out at a temperature of from 320°F (160°C) to 900°F (482°C) and a pressure of from 600 psig (4137 kPa-g) to 3000 psig (20684 kPa-g).

15. The process of claim 1, wherein the solvent component is comprised of trimethylbenzene.

16. The process of claim 7, wherein the solvent component is comprised of trimethylbenzene.

17. The process of claim 15, wherein the solvent component is comprised of at least 50 wt% trimethylbenzene, based on total weight of the solvent component.

18. The process of claim 16, wherein all of the supercritical hydrocarbon compounds each have a critical temperature of at least 300°F (149°C) and a critical pressure of less than or equal to 500 psig (3447 kPa-g).

19. The process of claim 1, wherein the heavy hydrocarbon oil component and the solvent component are combined prior to entering the hydroprocessing zone.

20. The process of claim 1, wherein the hydroprocessing zone contains the catalyst in a fixed bed, and the conditions in the hydroprocessing zone include a temperature of from 350°F (177°C) to 800°F (427°C), a total pressure

of from 800 psig (5516 kPa-g) to 1500 psig (10342 kPa-g), and a liquid hourly space velocity (LHSV) of the combined heavy hydrocarbon oil and solvent components of from 0.1 to 30 h⁻¹.