

METHOD FOR PRODUCING HIGH QUALITY BASE OILS USING TWO STAGE HYDROFINISHING**CROSS REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of priority to U.S. Provisional Appl. Ser. No. 63/138,810, filed on January 19, 2021, and to U.S. Patent Appl. Ser. No. 17/153,865, filed on January 20, 2021, the disclosures of which are herein incorporated in their entirety.

FIELD OF THE INVENTION

[0002] The present disclosure relates to methods for producing high quality base oils using, for example, novel multistage hydrofinishing methods.

BACKGROUND AND SUMMARY

[0003] Modern refining processes for producing lubricating oils from crudes typically use a number of hydrogen processes. The processes are employed to produce lubricating oils having suitable lubricating properties over a wide range of operating conditions. Hydrotreating/hydrocracking is generally an upgrading process for increasing viscosity index by removing low viscosity index molecules, including molecules containing sulfur and nitrogen. Hydrodewaxing is typically a process for improving the low temperature properties by isomerizing the long chain waxy molecules, if otherwise not removed, may have a negative impact on the pour and cloud points of the fractions. Hydrofinishing typically describes a process to further upgrade the lubricating base oil quality including color and oxidation stability often by saturating the aromatic molecules. However, in many cases the base oil still may have undesirable levels of aromatics, residual organic sulfur, and/or nitrogen. Accordingly, it would be desirable if additional or alternative processes were discovered for economically and efficiently producing base oil with one or more improved properties.

[0004] Advantageously, the instant processes economically and/or efficiently produce base oils with one more improved properties, e.g., lower aromatics. In one embodiment the process comprises a process for producing a low aromatic base oil comprising first contacting an SSZ-91 isomerized stream with a noble metal hydrofinishing catalyst under 1st hydrofinishing conditions to provide a 1st hydrofinished stream. Next, the 1st hydrofinished stream is contacted with a second noble metal hydrofinishing catalyst under 2nd hydrofinishing conditions to provide a 2nd hydrofinished stream. Typically, the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions.

[0005] In another embodiment, the application pertains to a process for producing a low aromatic base oil comprising first contacting a hydrocarbon feedstock with hydrogen and a catalyst comprising crystalline molecular sieve SSZ-91 and platinum under hydroisomerization dewaxing conditions to provide an isomerized stream. The isomerized stream is then contacted under 1st hydrofinishing

conditions with a catalyst comprising a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof. The catalyst may comprise a noble metal content from about 0.1 to about 0.6 wt. %. The 1st hydrofinished stream is then contacted under 2nd hydrofinishing conditions with a catalyst comprising a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof. The catalyst may comprise a noble metal content from about 0.1 to about 0.6 wt. %. Generally, the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions. Advantageously, a base oil is produced from the process that often comprises at least about 40% less aromatics by weight than a comparable process employing a single hydrofinishing step.

[0006] Further features of the disclosed design, and the advantages offered thereby, are explained in greater detail hereinafter with reference to specific example embodiments illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 depicts a simplified process flow scheme with one stage hydrofinishing.

[0008] Figure 2 depicts a simplified process flow scheme with two stage hydrofinishing.

DETAILED DESCRIPTION

[0009] Although illustrative embodiments of one or more aspects are provided herein, the disclosed processes may be implemented using any number of techniques. The disclosure is not limited to the illustrative or specific embodiments, drawings, and techniques illustrated herein, including any exemplary designs and embodiments illustrated and described herein, and may be modified within the scope of the appended claims along with their full scope of equivalents.

[0010] The following description of embodiments provides non-limiting representative examples referencing numerals to particularly describe features and teachings of different aspects of the invention. The embodiments described should be recognized as capable of implementation separately, or in combination, with other embodiments from the description of the embodiments. A person of ordinary skill in the art reviewing the description of embodiments should be able to learn and understand the different described aspects of the invention. The description of embodiments should facilitate understanding of the invention to such an extent that other implementations, not specifically covered but within the knowledge of a person of skill in the art having read the description of embodiments, would be understood to be consistent with an application of the invention.

Definitions

[0011] The following terms used herein have the meanings as defined herein below, unless otherwise indicated.

[0012] The term “hydrotreating” refers to processes or steps performed in the presence of hydrogen for the hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, and/or hydrodearomatization of components (e.g., impurities) of a hydrocarbon feedstock, and/or for the hydrogenation of unsaturated compounds in the feedstock. Depending on the type of hydrotreating and the reaction conditions, products of hydrotreating processes may have improved aromatic content, viscosities, viscosity indices, saturates content, low temperature properties, volatilities and depolarization, for example.

[0013] As used herein the term “molecular sieve” refers to a crystalline material containing pores, cavities, or interstitial spaces of a uniform size in which molecules small enough to pass through the pores, cavities, or interstitial spaces are adsorbed while larger molecules are not. Examples of molecular sieves include zeolites and non-zeolite molecular sieves such as zeolite analogs including, but not limited to, SAPOs (silicoaluminophosphates), MeAPOs (metalloaluminophosphates), AlPO_4 , and ELAPOs (nonmetal substituted aluminophosphate families).

[0014] As used herein, the term “pour point” refers to the temperature at which an oil will begin to flow under controlled conditions. The pour point may be determined by, for example, ASTM D5950.

[0015] “Target pour point” means the desired or required pour point of a lubricant base oil product. The target pour point is generally less than about -10°C , and typically in the range from about -10°C to -50°C and in some embodiments from about -5°C to about 20°C .

[0016] As used herein, “cloud point” refers to the temperature at which a lube oil sample begins to develop a haze as the oil is cooled under specified conditions. The cloud point of a lube base oil is complementary to its pour point. Cloud point may be determined by, for example, ASTM D5773.

[0017] The “pour point/cloud point spread,” or “pour-cloud spread” of a base oil, refers to the spread or difference between the cloud point and the pour point, and is defined as the cloud point minus the pour point, as measured in $^\circ\text{C}$. Generally, it is desirable to minimize the spread between the pour and cloud points.

[0018] The Periodic Table of the Elements referred to in this disclosure is the CAS version published by the Chemical Abstract Service in the Handbook of Chemistry and Physics, 72nd edition (1991-1992).

[0019] “Group VIII metal” refers to elemental metal(s) selected from Group VIII of the Periodic Table of the Elements and/or to metal compounds comprising such metal(s).

[0020] Unless otherwise specified, the “feed rate” of a hydrocarbon or other feedstock being fed to a catalytic reaction zone is expressed herein as the volume of feed per volume of catalyst per hour, which may be referred to as liquid hourly space velocity (LHSV) with units of reciprocal hours (h^{-1}).

[0021] The term "hydroisomerization" refers to a process in which n-paraffins (n-alkanes) are isomerized to their more branched counterparts in the presence of hydrogen over a hydroisomerization (dewaxing) catalyst.

[0022] Unless otherwise specified, the recitation of a genus of elements, materials, or other components from which an individual component or mixture of components can be selected is intended to include all possible sub-generic combinations of the listed components and mixtures thereof. Also, "include" and its variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that may also be useful in the materials, compositions, and methods of this invention.

Properties for the materials described herein may be determined in some embodiments as follows:

[0023] (a) $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio (SAR): determined by ICP elemental analysis. A SAR of infinity (∞) represents the case where there is no aluminum in the zeolite, i.e., the mole ratio of silica to alumina is infinity. In that case, the molecular sieve is comprised essentially of all silica.

[0024] (b) Surface area: determined by N_2 adsorption at its boiling temperature. BET surface area is calculated by the 5-point method at $P/P_0 = 0.050, 0.088, 0.125, 0.163, \text{ and } 0.200$. Samples are first pre-treated at 400°C for 6 hours in the presence of flowing, dry N_2 so as to eliminate any adsorbed volatiles like water or organics.

[0025] (c) Micropore volume: determined by N_2 adsorption at its boiling temperature. Micropore volume is calculated by the t-plot method at $P/P_0 = 0.050, 0.088, 0.125, 0.163, \text{ and } 0.200$. Samples are first pre-treated at 400°C for 6 hours in the presence of flowing, dry N_2 so as to eliminate any adsorbed volatiles like water or organics.

[0026] (d) Mesopore pore diameter: determined by N_2 adsorption at its boiling temperature. Mesopore pore diameter is calculated from N_2 isotherms by the BJH method described in E.P. Barrett, L.G. Joyner and P.P. Halenda, "The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms" J. Am. Chem. Soc. 1951 73, 373-380. Samples are first pre-treated at 400°C for 6 hours in the presence of flowing, dry N_2 so as to eliminate any adsorbed volatiles like water or organics.

[0027] (e) Total pore volume: determined by N_2 adsorption at its boiling temperature at $P/P_0 = 0.990$. Samples are first pre-treated at 400°C for 6 hours in the presence of flowing, dry N_2 so as to eliminate any adsorbed volatiles like water or organics.

[0028] (f) Aromatic weight percent is determined by UV absorption at wavelengths from 220nm to 400nm as in ASTM D2008.

[0029] Where permitted, all publications, patents and patent applications cited in this application are incorporated by reference herein in their entirety, to the extent such disclosure is not inconsistent with the present invention.

General Processes of the Present Application Using 1st and 2nd Hydrofinished Streams

[0030] The processes of the present application generally comprise hydrofinishing processes comprising two or more, or three or more stages or steps with varying conditions such as temperature to produce a low aromatic base oil. Typically, the processes comprise contacting an isomerized stream with a noble metal hydrofinishing catalyst under 1st hydrofinishing conditions to provide a 1st hydrofinished stream.

[0031] The 1st hydrofinished stream is then contacted with a second noble metal hydrofinishing catalyst under 2nd hydrofinishing conditions to provide a 2nd hydrofinished stream. The 1st and 2nd hydrofinishing conditions (and 3rd, 4th, or more if employed) may be selected from those conditions described below for hydrofinishing and may vary depending upon feedstocks and desired base oil product and properties.

[0032] While other 1st and 2nd hydrofinishing conditions such as pressure, feed rate, catalyst, and the like may be the same or different, typically in some embodiments of the instant application the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions. This often leads to the surprising and unexpected low amounts of aromatics in the base oils produced as shown in the below examples.

[0033] The difference in the temperature employed between the 1st and 2nd hydrofinishing may be selected based upon desired throughput, desired product and properties, equipment employed, and other process parameters. In some embodiments, the 2nd hydrofinishing conditions comprise a temperature lower than the 1st hydrofinishing conditions wherein the temperature of the 2nd hydrofinishing conditions may be lower than the 1st hydrofinishing conditions by at least about 80°F, or at least about 90°F, or at least about 100°F, or at least about 120°F, or at least about 140°F, or at least about 160°F, or at least about 180°F, or at least about 200°F, or at least about 220°F, or at least about 250°F up to at most about a temperature differential no higher than about 450°F, or no higher than about 350°F, or no higher than about 325°F, or no higher than about 300°F.

[0034] The specific temperature employed in the 1st hydrofinishing conditions and the specific lower temperature employed in the 2nd hydrofinishing conditions may vary depending upon desired throughput, desired product and properties, equipment employed, and other process parameters. Generally, the 1st hydrofinishing conditions may comprise a temperature of from about 475°F, or from about 500°F, or from about 510°F, or from about 520°F, or from about 530°F, or from about 540°F, or

from about 560°F, or from about 580°F, or from about 600°F, or from about 625°F, or from about 650°F up to about 800°F, or up to about 750°F, or up to about 700°F.

[0035] The 2nd hydrofinishing conditions generally comprise a lower temperature than the 1st hydrofinishing conditions and the specific lower temperature employed in the 2nd hydrofinishing conditions may vary as described above based on many factors. Typically, the 2nd hydrofinishing lower temperature conditions comprise a temperature differential as described above. In terms of absolute temperature for the 2nd hydrofinishing lower temperature conditions the temperature may include one of from about 370°F, or from about 380°F, up to about 390°F, or up to about 410°F, or up to about 430°F, or up to about 455°F, or up to about 460°F, or up to about 465°F.

[0036] In some embodiments by employing two or more hydrofinishing stages with subsequent lower temperatures a base oil with low aromatics may be obtained. That is, in some embodiments base oils produced by processes described herein may comprise less than about 0.9%, or less than about 0.8%, or less than about 0.7%, or less than about 0.6%, or less than about 0.5%, or less than about 0.4%, or less than about 0.3% by weight aromatics. In other embodiments, the total aromatics in a base oil produced by the process may be at least about 30% less, or at least about 35% less, or at least about 40% less, or at least about 45% less, or at least about 50% less than a comparable process employing a single hydrofinishing step.

[0037] Comparable processes employing a single hydrofinishing step include those such as shown in the comparable example wherein the single hydrofinishing step employs a temperature in its single stage that is the same, or within 2 degrees, or within 4 degrees, of the temperature employed in the 2nd hydrofinishing conditions. That is, the temperature employed in the 1st hydrofinishing conditions is higher than both the 2nd hydrofinishing conditions and the temperature in single hydrofinishing step while other conditions in the single and two or more step hydrofinishing steps are similar or the same.

[0038] Useful hydrofinishing conditions and catalysts for the 1st and 2nd hydrofinishing conditions, as well as isomerization prior to hydrofinishing are described below.

Hydrofinishing Units

[0039] The isomerization feedstock is typically fed to a one or more hydrofinishing units to make the 1st hydrofinished stream and 2nd hydrofinishing stream and ultimately to provide a suitable quality and yield of the desired base oil product. Such a hydrofinishing step or steps, may remove traces of any aromatics, olefins, color bodies, and the like from the base oil product. The hydrofinishing unit may include a hydrofinishing catalyst comprising a silica alumina support and a noble metal, typically palladium, or platinum in combination with palladium. In an embodiment, the noble metal content of the hydrofinishing catalyst may typically be in the range from about 0.1 to about 1.0 wt. %, usually from about 0.1 to about 0.6 wt. %, and often from about 0.2 to about 0.5 wt. %. The isomerized stream and

the hydrofinished streams may be contacted with the first and second catalyst in the same hydrofinishing unit or separate units in series. The catalyst contacted with the isomerized stream and the catalyst contacted with the 1st hydrofinished stream may be the same or different catalysts.

[0040] Hydrofinishing may be performed in the presence of a hydrogenation catalyst which may also be referred to as a hydrofinishing catalyst, as is known in the art. The hydrogenation catalyst used for hydrofinishing may comprise, for example, platinum, palladium, or a combination thereof on a silica alumina support. The hydrofinishing may be performed at a temperature in the range from about 400°F to about 650°F (204°C to 343°C), and a pressure in the range from about 400 psig to about 4000 psig (2.76 to 27.58 MPa). Hydrofinishing for the production of lubricating oils is described, for example, in U.S. Patent No. 3,852,207, the disclosure of which is incorporated by reference herein.

[0041] Within the reactor, the feed may be contacted with a hydrotreating catalyst under hydrotreating conditions. Contacting the feedstock with the hydrotreating catalyst serve to effectively hydrogenate aromatics in the feedstock, and in some cases remove some N- and S- containing compounds from the feed. By "effectively hydrogenate aromatics" is meant that the hydrotreating catalyst is able to decrease the aromatic content of the feedstock by at least about 20%. The hydrotreated feedstock may generally comprise C₁₀₊ n-paraffins and slightly branched iso-paraffins, with a wax content of typically at least about 20%. The hydrotreated feedstock may first be contacted with the hydroisomerization catalyst under hydroisomerization dewaxing conditions to provide an isomerization stream. The hydrotreating and hydroisomerization conditions that may be used for catalytic dewaxing processes of the present invention are described herein below.

Hydrofinishing Catalysts

[0042] In an embodiment, catalyst systems of the present invention may include a hydrofinishing which also may be referred to hydrotreating or hydrogenation catalyst. Hydrotreating catalysts useful in the present invention may comprise a refractory inorganic oxide support and a Group VIII metal. The oxide support may also be referred to herein as a binder. The support of the hydrotreating catalyst may be prepared from or comprise alumina, silica, silica/alumina, titania, magnesia, zirconia, and the like, or combinations thereof. The catalyst support may comprise amorphous materials, crystalline materials, or combinations thereof. Examples of amorphous materials include, but are not limited to, amorphous alumina, amorphous silica, amorphous silica- alumina, and the like.

[0043] In an embodiment, the support may comprise amorphous alumina. When using a combination of silica and alumina, the distribution of silica and alumina in the support may be either homogeneous or heterogeneous. In some embodiments, the support may consist of an alumina gel in which is dispersed the silica, silica/alumina, or alumina base material. The support may also contain refractory materials other than alumina or silica, such as for example other inorganic oxides or clay particles,

provided that such materials do not adversely affect the hydrogenation activity of the final catalyst or lead to deleterious cracking of the feedstock.

[0044] In a sub-embodiment, silica and/or alumina will generally comprise at least about 90 wt.% of the support of the hydrotreating catalyst, and in some embodiments the support may be at least substantially all silica or all alumina. Regardless of the type of support material in the hydrotreating catalyst, the hydrotreating catalyst used in processes and catalyst systems of the present invention will typically have low acidity. Where appropriate, the acidity of the support can be decreased by treatment with alkali and/or alkaline earth metal cations.

[0045] Various crystalline and non-crystalline catalyst support materials that may be used in practicing the present invention, as well as the quantification of their acidity levels and methods for neutralizing acid sites in the catalyst support, are described in co-pending, commonly assigned U.S. Patent Application Publication No. 2011/0079540, the disclosure of which is incorporated by reference herein in its entirety.

[0046] The Group VIII metal component(s) of the hydrotreating catalyst may comprise platinum, palladium, or combinations thereof. In an embodiment, the hydrotreating catalyst comprises platinum and palladium with a Pt:Pd ratio in the range from about 5 : 1 to about 1 : 5, typically from about 3 : 1 to about 1 : 3, and often from about 1 : 1 to about 1 : 2. The Group VIII metal content of the hydrotreating catalyst may generally be in the range from about 0.01 wt. % to about 5 wt. %, typically from about 0.2 wt. % to about 2 wt. %. In an embodiment, the hydrotreating catalyst may comprise platinum at a concentration in the range from about 0.1 to about 1.0 wt. %, and palladium at a concentration in the range from about 0.2 to about 1.5 wt.%.

[0047] In a sub-embodiment, the hydrotreating catalyst may comprise about 0.3 wt. % platinum and about 0.6 wt. % palladium. Hydrotreating catalysts of the present invention generally exhibit sulfur tolerance as well as high catalytic activity.

[0048] In an embodiment, the Group VIII metal of the hydrotreating catalyst may be dispersed on the inorganic oxide support. A number of methods are known in the art to deposit platinum and/or palladium metal, or compounds comprising platinum and/or palladium, onto the support; such methods include ion exchange, impregnation, and co-precipitation. In an embodiment, the impregnation of the support with platinum and/or palladium metal may be performed at a controlled pH value. The platinum and/or palladium is typically added to the impregnating solution as a metal salt, such as a halide salt, and/or an amine complex, and/or a salt of a mineral acid. Ammonium salts have been found to be particularly useful in preparing solutions for Group VIII metal impregnation. Other examples of metal salts that may be used include nitrates, carbonates, and bicarbonates, as well as carboxylic acid salts such as acetates, citrates, and formates.

[0049] Optionally, the impregnated support may be allowed to stand with the impregnating solution, e.g., for a period in the range from about 2 to about 24 hours. Following impregnation of the oxide support with the Group VIII metal, the impregnated support can be dried and/or calcined. After the hydrotreating catalyst has been dried and calcined, the prepared catalyst may be reduced with hydrogen, as is conventional in the art, and placed into service.

[0050] Typically, the hydrotreating catalyst may comprise from about 5% to about 20% of the total catalyst volume, and usually from about 5% to about 15% of the total catalyst volume.

Isomerized Stream, Catalysts and Reaction Conditions

[0051] Generally, the isomerized stream for the 1st hydrofinishing step may be obtained in any convenient manner which may vary depending upon the specific conditions of the feedstock, the desired properties for the base oil, and other factors. The isomerization streams that are useful are not particularly limited and may vary depending upon the desired product, isomerization, hydrofinishing, and/or other conditions, catalysts employed, and so forth. Isomerization conditions and catalysts may vary widely. Typically, a hydrocarbon feedstock is contacted with the hydroisomerization catalyst under hydroisomerization dewaxing conditions to provide an isomerization stream. The isomerized stream may be produced by contacting a hydrocarbon feedstock with hydrogen and a noble metal hydroisomerization catalyst under hydroisomerization dewaxing conditions to provide the isomerized stream.

[0052] The noble metal hydroisomerization catalyst may vary but in some embodiments comprises a crystalline molecular sieve SSZ-91 and platinum. Such SSZ-91 catalysts are described in detail in U.S. Patent No. 10,618,816 entitled "Molecular sieve SSZ-91, methods for preparing SSZ-91, and uses for SSZ-91" which is incorporated herein by reference. Similarly, the hydroisomerization dewaxing conditions may vary but in some embodiments comprise a temperature of from about 550°F to about 700°F, and preferably from 590°F to about 675°F. In some embodiments the hydroisomerization dewaxing conditions comprise a pressure in the range from about 15 to about 3000 psig and preferably in the range from about 100 to about 2500 psig.

[0053] The hydroisomerization dewaxing conditions may comprise a hydrocarbon feedstock feed rate in the range of from about 0.1 to about 20 hr⁻¹ LHSV in the presence of hydrogen wherein the hydrogen to hydrocarbon ratio is in a range from about 2000 to about 10,000 standard cubic feet per barrel hydrocarbon. In other embodiments the hydrocarbon feedstock feed rate may be from about 0.1 to about 5 hr⁻¹ LHSV. The hydrogen to hydrocarbon ratio may be from about 2500 to about 5000 standard cubic feet per barrel hydrocarbon in some embodiments.

[0054] The hydroisomerization catalysts may comprise a 1-D, 10-ring molecular sieve and a Group VIII metal, e.g., substantially as described herein above under "Hydroisomerization Catalysts." The

hydroisomerization catalysts may be selective for the isomerization of n-paraffins in the feedstock, such that feedstock components are preferentially isomerized rather than cracked.

Hydroisomerization Catalysts

[0055] In an embodiment, processes of the present invention use a hydroisomerization catalyst selective for the isomerization of n-paraffins in the hydrocarbon feed. Useful hydroisomerization catalysts may comprise a molecular sieve and a Group VIII metal. In an embodiment, the molecular sieve of the hydroisomerization catalyst may comprise a 1-D, 10-ring molecular sieve. The Group VIII metal of the first and second hydroisomerization catalysts may comprise platinum, palladium, or a combination thereof. In an embodiment, the hydroisomerization catalysts may comprise from about 0.1 to about 1.5 wt. % of the Group VIII metal, typically from about 0.2 to about 1.0 wt. %, and usually from about 0.325 to about 1.0 wt. % of the Group VIII metal. In an embodiment, the hydroisomerization catalysts may further comprise a metal modifier selected from the group consisting of Mg, Ca, Sr, Ba, K, La, Pr, Nd, Cr, and combinations thereof, substantially as described herein below.

[0056] Typically, the hydroisomerization catalysts will still further comprise a support or binder. The support may comprise a refractory inorganic oxide. Suitable inorganic oxide supports for the hydroisomerization catalysts include silica, alumina, titania, magnesia, zirconia, silica-alumina, silica-magnesia, silica-titania, and the like, and combinations thereof. The hydroisomerization catalysts may comprise from about 5 to about 95 wt. % or more of the molecular sieve component, typically from about 15 to about 85 wt. % of the molecular sieve, and usually from about 25 to about 75 wt. % of the molecular sieve. Generally, it is advantageous to minimize the molecular sieve component for economic reasons, provided that the catalyst retains the required activity and selectivity levels. The hydroisomerization catalysts may comprise from about 0 to about 95 wt. % of the support material, and more typically from about 5 to about 90 wt. %.

[0057] In an exemplary catalyst system for dewaxing hydrocarbon feedstocks according to processes of the present invention, each the hydroisomerization catalyst may comprise a 1-D, 10-ring molecular sieve and a Group VIII metal. The molecular sieve of the hydroisomerization catalysts may comprise a medium pore zeolite, e.g., a zeolite having a pore aperture in the range from about 0.39 nm to about 0.7 nm. In an embodiment, each of the hydroisomerization catalysts may further comprise from about 0.325 wt. % to about 1 wt. % platinum.

[0058] Examples of molecular sieves that may be useful in formulating hydroisomerization catalysts include molecular sieves of the AEL framework type code, such as SAPO-11, SAPO-31, SM-3, SM-6; as well as zeolite type materials of the MTT or TON codes. Molecular sieves of the MTT code include ZSM-23, SSZ-32, EU-13, ISI-4, and KZ-1. Molecular sieves of the TON code that may be useful in practicing the present invention include Theta-1, ISI-1, KZ-2, NU-10, and ZSM-22. The parameters of MTT and TON

type molecular sieves are further described in the Atlas of Zeolite Framework Types which is published by the International Zeolite Association (IZA). In an embodiment, the hydroisomerization catalysts contain zeolite SSZ-32. In a sub-embodiment, the hydroisomerization catalysts contain SSZ-32. Processes of the present invention are not limited to any particular hydroisomerization catalyst formulations.

Metal Loading of Catalysts

[0059] In an embodiment, the hydroisomerization catalysts may further comprise one or more metal modifier(s). Typically, the metal modifier(s) may be selected from the group consisting of Mg, Ca, Sr, Ba, K, La, Pr, Nd, Cr, and combinations thereof. In a sub-embodiment, the metal modifier may comprise Mg. As a non-limiting example, the hydroisomerization catalysts may comprise a 1-D, 10-ring molecular sieve, such as SSZ-32; a Group VIII noble metal, such as platinum; and in some embodiments a metal modifier such as magnesium. In an embodiment, a metal-modified catalyst of the present invention may comprise from about 0.5 to about 3.5 wt. % of Mg or other metal modifier(s), typically from about 0.5 to about 2.5 wt. %, and usually from about 0.9 to about 2.5 wt. % of Mg or other metal modifier(s).

[0060] In formulating a catalyst or catalyst system for dewaxing processes of the present invention, a mixture of a molecular sieve and an oxide binder may be formed into a particle or extrudate having a wide range of physical shapes and dimensions. In an embodiment, the extrudate or particle may be dried and calcined prior to metal loading. Calcination may be performed at temperatures typically in the range from about 390°F to about 1100°F (199°C to 593°C) for periods of time ranging from about 0.5 to about 5 hours, or more. The calcined extrudate or formed particle may then be loaded with at least one metal modifier selected from the group consisting of Ca, Cr, Mg, La, Na, Pr, Sr, K, Nd, and combinations thereof. While not being bound by theory, such metals may effectively reduce the number of acid sites on the molecular sieve of the metal-modified hydroisomerization catalyst, thereby increasing the catalyst's selectivity for isomerization (versus cracking) of n-paraffins in the feed. The loading of modifying metal(s) on the catalyst(s) may be accomplished by techniques known in the art, such as by impregnation or ion exchange. Ion exchange techniques typically involve contacting the extrudate or particle with a solution containing a salt of the desired metal cation(s). A variety of metal salts, such as halides, nitrates, and sulfates, may be used in this regard. Following contact with a salt solution of the desired metal cation(s), the extrudate or particle may be dried, e.g., at temperatures in the range from about 150°F to about 800°F (66°C to 427°C). The extrudate or particle may thereafter be further loaded with a Group VIII metal component of the catalyst.

[0061] In an embodiment, a molecular sieve or catalyst of the invention may be co-impregnated with a modifying metal and a Group VIII metal. After loading the Group VIII and modifying metals, the catalyst may be calcined in air or inert gas at temperatures in the range from about 500°F to about 900°F (260°C

to 482°C). The preparation of molecular sieve catalysts comprising a metal modifier is disclosed in commonly assigned U.S. Patent No. 7,141,529 and in U.S. Patent Application Publication No. 2008/0083657, the disclosure of each of which is incorporated by reference herein in its entirety.

Isomerization and Hydrofinishing Reaction Conditions

[0062] The conditions under which processes of the present invention are carried out will generally include a temperature within a range from about 390°F to about 800°F (199°C to 427°C). In an embodiment, the hydroisomerization dewaxing conditions includes a temperature in the range from about 550°F to about 700°F (288°C to 371°C). In a further embodiment, the temperature may be in the range from about 590°F to about 675°F (310°C to 357°C). The pressure may be in the range from about 15 to about 3000 psig (0.10 to 20.68 MPa), and typically in the range from about 100 to about 2500 psig (0.69 to 17.24 MPa).

[0063] Typically, the feed rate to the catalyst system/reactor during dewaxing processes of the present invention may be in the range from about 0.1 to about 20 hr⁻¹ LHSV, and usually from about 0.1 to about 5 hr⁻¹ LHSV. Generally, dewaxing processes of the present invention are performed in the presence of hydrogen. Typically, the hydrogen to hydrocarbon ratio may be in a range from about 2000 to about 10,000 standard cubic feet per barrel hydrocarbon, and usually from about 2500 to about 5000 standard cubic feet per barrel hydrocarbon.

[0064] The above conditions may apply to the hydrotreating conditions of the hydrotreating zone as well as to the hydroisomerization conditions of the hydroisomerization zones. The reactor temperature and other process parameters may vary according to factors such as the nature of the hydrocarbon feedstock used and the desired characteristics (e.g., pour point, cloud point, VI) and yield of the base oil product.

[0065] The hydroisomerization catalysts may comprise a 1-D, 10-ring molecular sieve and a Group VIII metal, e.g., substantially as described herein above under "Hydroisomerization Catalysts." The hydroisomerization catalysts may be selective for the isomerization of n-paraffins in the feedstock, such that feedstock components are preferentially isomerized rather than cracked.

Base Oil Products

[0066] The base oil product may have a pour point not higher than about -9°C, typically not higher than about -12°C, and usually not higher than about -14°C. The base oil product may have a cloud point not higher than about -5°C, typically not higher than about -7°C, and usually not higher than about -12°C. The base oil product may have a pour-cloud spread of not more than about 7°C, typically not more than about 5°C, and usually not more than about 3°C. In an embodiment, the base oil product having the above properties may be obtained at a yield of at least about 89%.

[0067] In some embodiments, processes of the invention provide a high value, high quality lubricant oil in good yield from a low value waxy hydrocarbon feedstock. The lubricant oils of may have a pour point less than about -9°C, usually less than about -12°C, and often less than about -14°C, e.g., as measured by ASTM D97. In an embodiment, the lubricant oil product may have a pour point in the range from about -10°C to about -30°C. The products may have viscosities in the range of 3 to 30 cSt at 100°C, and a VI in the range from about 95 to about 170 as measured by ASTM D445.

Feed for Base Oil Production

[0068] The instant invention may be used with a wide variety of hydrocarbon feedstocks, including whole crude petroleum, reduced crudes, vacuum tower residua, cycle oils, synthetic crudes, gas oils, vacuum gas oils, foots oils, Fischer-Tropsch derived waxes, and the like. In an embodiment, the hydrocarbon feedstocks can be described as waxy feeds having pour points generally above about 0°C, and having a tendency to solidify, precipitate, or otherwise form solid particulates upon cooling to about 0°C. Straight chain n-paraffins, either alone or with only slightly branched chain paraffins, having 16 or more carbon atoms may be referred to herein as waxes. The feedstock will usually be a C₁₀₊ feedstock generally boiling above about 350°F (177°C).

[0069] In an embodiment, the feedstock may comprise a heavy feed. Herein, the term "heavy feed" may be used to refer to a hydrocarbon feedstock wherein at least about 80% of the components have a boiling point above about 900°F (482°C). Examples of heavy feeds suitable for practicing the present invention include heavy neutral (600N) and bright stock.

[0070] In an embodiment, the hydrocarbon feedstocks of the present invention may generally have a pour point above 0°C, and in some embodiments above about 20°C. In contrast, the base oil products of processes of the present invention, generally have pour points below 0°C, typically below about -12°C, and often below about -14°C.

[0071] In an embodiment, the feedstock employed in processes of the present invention can be a waxy feed which contains more than about 20% wax, more than about 50% wax, or even greater than about 70% wax. More typically, the feed will contain from about 5% to about 30% wax. As used herein, the term "waxy hydrocarbon feedstocks" may include plant waxes and animal derived waxes in addition to petroleum derived waxes.

[0072] According to one aspect of the present invention, a wide range of feeds may be used to produce lubricant base oils in high yield with good performance characteristics, including low aromatics, low pour point, low cloud point, low pour-cloud spread, and high viscosity index. The quality and yield of the lube base oil product of the instant invention may depend on a number of factors, including, but not limited to, the hydrofinishing steps and conditions described herein.

EXAMPLES

Comparative Example

[0073] A comparative example was run using dewaxing 101 and one stage hydrofinishing 102 followed by product separation systems 201, 202 and 203 as shown in Figure 1. A noble metal hydroisomerization catalyst was installed in 101. This noble metal catalyst was composited with crystallite SSZ-91 and platinum. The 2nd reactor 102 (one stage hydrofinishing) was loaded with a Pd/Pt catalyst to further improve the lube product quality.

[0074] Key for Figure 1: 101-dewaxing; 102-one stage hydrofinishing; 201-High pressure separator; 202-Distillation system; 203-Debutanizer

[0075] A “heavy neutral” feed was used to evaluate this process configuration and the properties are described in Table 1 below. The feed and reaction conditions are described in WO2012/005980 which is incorporated herein by reference.

Table 1 Feed Properties

Property	Value
API Gravity	29.6
N, ppm	1
S, ppm	32
Aromatics, lv%	18
SIMDIST TBP (WT%), °F	
TBP @0.5	716
TBP @5	808
TBP @10	842
TBP @30	909
TBP @50	950
TBP @70	990
TBP @90	1043
TBP @95	1065
TBP @99.5	1110

[0076] The reaction was performed in a micro unit with the described configuration and the run was operated under 2100 psig total pressure. Prior to the introduction of feed, the catalysts were activated by a standard reduction procedure. The HN feed was passed through the hydrodewaxing reactor at a LHSV of 1.2 hr⁻¹ and then hydrofinished in 102. The hydrogen to oil ratio was about 3000 scfb. The base oil product was separated from fuels through the distillation section. Product aromatics content was determined.

[0077] 101 was operated at 600-650°F to convert the wax molecules to reach the product pour point target and 201 was operated at 450°F to improve the product quality. The result is shown in Table 2 below.

Example 1

[0078] Example 1 consists of dewaxing 101, two stage hydrofinishing 102 and 103 followed by product separation systems 201, 202 and 203 as shown in Figure 2. A noble metal hydroisomerization catalyst was installed in the 1st stage reactor. After passing the dewaxing reactor, the effluent was first treated in 102 and then sent to 103 for further finishing. Both 102 and 103 were loaded with a Pd/Pt catalyst to saturate the aromatics and further remove the impurities. The hydrogen to oil ratio was about 3000 scfb. The lube product was separated from fuels through the distillation section. Product aromatics content was determined.

[0079] Key for Figure 2: 101-dewaxing; 102-1st stage hydrofinishing; 103-2nd stage hydrofinishing; 201-High pressure separator; 202-Distillation system; 203-Debutanizer

[0080] In Example 1 101 was operated at 600-650°F to convert the wax molecules to reach the product pour point target. 102 was operated at ~500°F and 103 was operated at 450°F to saturate the single-ring and multi-ring aromatics to improve the product quality and stability.

[0081] Examples 2-9 below were conducted in the same manner except that the temperatures were varied as described below. The results are shown in Table 2 below and Figure 3.

Example 2:

[0082] 102 was operated at ~510°F and 103 was operated at 400°F on the catalyst and process system of example 1.

Example 3:

[0083] 102 was operated at ~550°F and 103 was operated at 400°F on the catalyst and process system of example 1.

Example 4:

[0084] 102 was operated at ~550°F and 103 was operated at 370°F on the catalyst and process system of example 1.

Example 5:

[0085] 102 was operated at ~580°F and 103 was operated at 380°F on the catalyst and process system of example 1.

Example 6:

[0086] 102 was operated at ~600°F and 103 was operated at 380°F on the catalyst and process system of example 1.

Example 7:

[0087] 102 was operated at ~625°F and 103 was operated at 380°F on the catalyst and process system of example 1.

Example 8:

[0088] 102 was operated at ~625°F and 103 was operated at 410°F on the catalyst and process system of example 1.

Example 9:

[0089] 102 was operated at ~650°F and 103 was operated at 410°F on the catalyst and process system of example 1.

Table 2 – Results of Comparative and Examples 2-9

Examples	Comparative	1	2	3	4	5	6	7	8	9
1st stage HDF CAT, °F	450	500	510	550	550	580	600	625	625	650
2nd stage HDF CAT, °F		450	400	400	370	380	380	380	410	410
base oil product aromatics, wt%	0.93	0.8	0.81	0.67	0.55	0.61	0.53	0.52	0.35	0.38

Systems

[0090] Systems that are employed in the above-described processes and examples are also contemplated by the present application and are further described below in the following numbered embodiments.

[0091] 1. A system for producing a low aromatic base oil comprising:

an isomerization zone comprising a noble metal SSZ-91 hydroisomerization catalyst for producing an SSZ-91 isomerized stream;

a first hydrofinishing zone for contacting the SSZ-91 isomerized stream with a noble metal hydrofinishing catalyst under 1st hydrofinishing conditions to provide a 1st hydrofinished stream; and

a second hydrofinishing zone for contacting the 1st hydrofinished stream with a second noble metal hydrofinishing catalyst under 2nd hydrofinishing conditions to provide a 2nd hydrofinished stream wherein the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions.

[0092] 2. The system of embodiment 1, wherein a base oil produced by the system comprises less than 0.9% by weight aromatics.

[0093] 3. The system of embodiment 1, wherein a base oil produced by the system comprises a pour point of from about -5°C to about -20°C.

[0094] 4. The system of embodiment 1, wherein the total aromatics in a base oil produced by the system are at least about 30% less than a comparable system employing a single hydrofinishing step.

- [0095] 5. The system of embodiment 1, wherein the SSZ-91 isomerized stream is produced by contacting a hydrocarbon feedstock with hydrogen and a noble metal SSZ-91 hydroisomerization catalyst under hydroisomerization dewaxing conditions to provide the isomerized stream.
- [0096] 6. The system of embodiment 5, wherein the noble metal SSZ-91 hydroisomerization catalyst comprises a crystalline molecular sieve SSZ-91 and platinum.
- [0097] 7. The system of embodiment 1, wherein the noble metal hydrofinishing catalyst and second noble metal hydrofinishing catalyst each comprise a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof.
- [0098] 8. The system of embodiment 1, wherein the noble metal hydrofinishing catalyst and second noble metal hydrofinishing catalyst are the same.
- [0099] 9. The system of embodiment 1, wherein the noble metal hydrofinishing catalyst and second noble metal hydrofinishing catalyst each comprise a noble metal content from about 0.1 to about 1.0 wt. %.
- [00100] 10. The system of embodiment 1, wherein the 1st hydrofinishing conditions comprise a temperature of from about 475°F to about 700°F.
- [00101] 11. The system of embodiment 1, wherein the 2nd hydrofinishing conditions comprise a temperature of from about 370°F to about 475°F.
- [00102] 12. The system of embodiment 5, wherein the hydroisomerization dewaxing conditions comprise a temperature of from about 550°F to about 700°F.
- [00103] 13. The system of embodiment 5, wherein the hydroisomerization dewaxing conditions comprise a pressure in the range from about 15 to about 3000 psig.
- [00104] 14. The system of embodiment 5, wherein the hydroisomerization dewaxing conditions comprise a hydrocarbon feedstock feed rate in the range of from about 0.1 to about 20 hr⁻¹ LHSV in the presence of hydrogen wherein the hydrogen to hydrocarbon ratio is in a range from about 2000 to about 10,000 standard cubic feet per barrel hydrocarbon.
- [00105] 15. The system of embodiment 1, wherein the 1st hydrofinishing conditions and 2nd hydrofinishing conditions comprise a pressure in the range from about 15 to about 3000 psig.
- [00106] 16. The system of embodiment 1, wherein the 1st hydrofinishing conditions and 2nd hydrofinishing conditions comprise a 1st hydrofinished stream feed rate and 2nd hydrofinished stream feed rate of from about 0.1 to about 20 hr⁻¹ LHSV.
- [00107] 17. A system for producing a low aromatic base oil comprising:
an isomerization zone for contacting a hydrocarbon feedstock with hydrogen and a catalyst comprising crystalline molecular sieve SSZ-91 and platinum under hydroisomerization dewaxing conditions to provide an isomerized stream;

a first hydrofinishing zone for contacting the isomerized stream with a catalyst comprising a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof wherein the catalyst comprises a noble metal content from about 0.1 to about 0.6 wt. % under 1st hydrofinishing conditions to provide a 1st hydrofinished stream; and

a second hydrofinishing zone for contacting the 1st hydrofinished stream with a catalyst comprising a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof wherein the catalyst comprises a noble metal content from about 0.1 to about 0.6 wt. % under 2nd hydrofinishing conditions to provide a 2nd hydrofinished stream wherein the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions and wherein a base oil produced from the system comprises at least about 40% less aromatics by weight than a comparable system employing a single hydrofinishing step.

[00108] 18. The system of embodiment 17, wherein a base oil produced by the system comprises less than 0.8% by weight aromatics.

[00109] 19. The system of embodiment 17, wherein a base oil produced by the system comprises a pour point of not more than about -12°C.

[00110] 20. The system of embodiment 17, wherein the base oil product is obtained at a yield of at least about 85%.

[00111] 21. The system of embodiment 17 wherein the 2nd hydrofinishing conditions comprise a temperature which is from about 50 to about 450°F lower than the 1st hydrofinishing conditions.

[00112] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as may be apparent. Functionally equivalent methods and systems within the scope of the disclosure, in addition to those enumerated herein, may be apparent from the foregoing representative descriptions. Such modifications and variations are intended to fall within the scope of the appended representative claims. The present disclosure is to be limited only by the terms of the appended representative claims, along with the full scope of equivalents to which such representative claims are entitled. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[00113] The foregoing description, along with its associated embodiments, has been presented for purposes of illustration only. It is not exhaustive and does not limit the invention to the precise form disclosed. Those skilled in the art may appreciate from the foregoing description that modifications and variations are possible in light of the above teachings or may be acquired from practicing the disclosed embodiments. For example, the steps described need not be performed in the same sequence discussed

or with the same degree of separation. Likewise various steps may be omitted, repeated, or combined, as necessary, to achieve the same or similar objectives. Accordingly, the invention is not limited to the above-described embodiments, but instead is defined by the appended claims in light of their full scope of equivalents.

[00114] In the preceding specification, various preferred embodiments have been described with references to the accompanying drawings. It may, however, be evident that various modifications and changes may be made thereto, and additional embodiments may be implemented, without departing from the broader scope of the invention as set forth in the claims that follow. The specification and drawings are accordingly to be regarded as an illustrative rather than restrictive sense.

WHAT IS CLAIMED IS:

1. A process for producing a low aromatic base oil comprising:
contacting an SSZ-91 isomerized stream with a noble metal hydrofinishing catalyst under 1st hydrofinishing conditions to provide a 1st hydrofinished stream; and
contacting the 1st hydrofinished stream with a second noble metal hydrofinishing catalyst under 2nd hydrofinishing conditions to provide a 2nd hydrofinished stream;
wherein the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions.
2. The process of claim 1, wherein a base oil produced by the process comprises less than 0.9% by weight aromatics.
3. The process of claim 1, wherein a base oil produced by the process comprises a pour point of from about -5°C to about -20°C.
4. The process of claim 1, wherein the total aromatics in a base oil produced by the process are at least about 30% less than a comparable process employing a single hydrofinishing step.
5. The process of claim 1, wherein the SSZ-91 isomerized stream is produced by contacting a hydrocarbon feedstock with hydrogen and a noble metal SSZ-91 hydroisomerization catalyst under hydroisomerization dewaxing conditions to provide the isomerized stream.
6. The process of claim 5, wherein the noble metal SSZ-91 hydroisomerization catalyst comprises a crystalline molecular sieve SSZ-91 and platinum.
7. The process of claim 1, wherein the noble metal hydrofinishing catalyst and second noble metal hydrofinishing catalyst each comprise a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof.
8. The process of claim 1, wherein the noble metal hydrofinishing catalyst and second noble metal hydrofinishing catalyst are the same.
9. The process of claim 1, wherein the noble metal hydrofinishing catalyst and second noble metal hydrofinishing catalyst each comprise a noble metal content from about 0.1 to about 1.0 wt. %.
10. The process of claim 1, wherein the 1st hydrofinishing conditions comprise a temperature of from about 475°F to about 700°F.
11. The process of claim 1, wherein the 2nd hydrofinishing conditions comprise a temperature of from about 370°F to about 475°F.
12. The process of claim 5, wherein the hydroisomerization dewaxing conditions comprise a temperature of from about 550°F to about 700°F.
13. The process of claim 5, wherein the hydroisomerization dewaxing conditions comprise a pressure in the range from about 15 to about 3000 psig.

14. The process of claim 5, wherein the hydroisomerization dewaxing conditions comprise a hydrocarbon feedstock feed rate in the range of from about 0.1 to about 20 hr⁻¹ LHSV in the presence of hydrogen wherein the hydrogen to hydrocarbon ratio is in a range from about 2000 to about 10,000 standard cubic feet per barrel hydrocarbon.
15. The process of claim 1, wherein the 1st hydrofinishing conditions and 2nd hydrofinishing conditions comprise a pressure in the range from about 15 to about 3000 psig.
16. The process of claim 1, wherein the 1st hydrofinishing conditions and 2nd hydrofinishing conditions comprise a 1st hydrofinished stream feed rate and 2nd hydrofinished stream feed rate of from about 0.1 to about 20 hr⁻¹ LHSV.
17. A process for producing a low aromatic base oil comprising:
- contacting a hydrocarbon feedstock with hydrogen and a catalyst comprising crystalline molecular sieve SSZ-91 and platinum under hydroisomerization dewaxing conditions to provide an isomerized stream;
 - contacting the isomerized stream with a catalyst comprising a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof wherein the catalyst comprises a noble metal content from about 0.1 to about 0.6 wt. % under 1st hydrofinishing conditions to provide a 1st hydrofinished stream; and
 - contacting the 1st hydrofinished stream with a catalyst comprising a silica alumina support and a noble metal selected from palladium, platinum, or a combination thereof wherein the catalyst comprises a noble metal content from about 0.1 to about 0.6 wt. % under 2nd hydrofinishing conditions to provide a 2nd hydrofinished stream;
 - wherein the 2nd hydrofinishing conditions comprise a lower temperature than the 1st hydrofinishing conditions; and
 - wherein a base oil produced from the process comprises at least about 40% less aromatics by weight than a comparable process employing a single hydrofinishing step.
18. The process of claim 17, wherein a base oil produced by the process comprises less than 0.8% by weight aromatics.
19. The process of claim 17, wherein a base oil produced by the process comprises a pour point of not more than about -12°C.
20. The process of claim 17, wherein the base oil product is obtained at a yield of at least about 85%.
21. The process of claim 17 wherein the 2nd hydrofinishing conditions comprise a temperature which is from about 50 to about 450°F lower than the 1st hydrofinishing conditions.