

CATALYTIC AND SOLVENT PROCESSING FOR BASE OIL PRODUCTIONFIELD

[0001] Systems and methods are provided for production of lubricant oil basestocks by a combination of catalytic and solvent processing.

BACKGROUND

[0002] Dewaxing is a commonly used technique for improving the properties of a petroleum fraction for use in various products, such as fuels or lubricant base stocks. Historically, solvent dewaxing was the first type of dewaxing used for modifying the properties of a feedstock. Solvent extraction and dewaxing allowed for separation of a feedstock into a raffinate fraction for use as a distillate fuel or lubricant, an aromatics fraction, and a waxy fraction. More recently, catalytic dewaxing has been commonly used for improving the properties of feeds for use in fuels or lubricant base stocks.

[0003] U.S. Patent 4,259,170 describes a process for manufacturing lube basestocks. In the process, one or more lower boiling fractions from a vacuum distillation tower are solvent dewaxed to form lubricant base stocks. One or more higher boiling fractions are catalytically dewaxed in order to provide a pour point improvement for the higher boiling fractions that is greater than the amount that can be achieved by solvent dewaxing.

[0004] U.S. Patent 6,773,578 describes a process for preparing lubes with high viscosity index values. The process includes obtaining a first feedstock that includes at least 95% of material that boils below 1150°F (621°C), and a second feedstock that includes at least 95% of material that boils above 1150°F (621°C).

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The feedstock containing the portion that boils below 1150°F is catalytically dewaxed. The feedstock containing the portion that boils above 1150°F is solvent dewaxed and optionally also catalytically dewaxed. Performing solvent dewaxing on the above 1150°F portion is described as reducing the difference between the cloud point and the pour point for the resulting products.

[0005] U.S. Patent Application Publication 2014/0042056 describes a process for preparing multiple base oils from a feedstock. A lower boiling portion of a feedstock is catalytically dewaxed to form light neutral base oil(s) while a higher boiling portion of a feedstock is solvent processed to form heavy neutral or brightstock base oil(s).

[0006] U.S. Patent 6,592,748 describes a raffinate hydroconversion process. After solvent extraction, the raffinate is exposed to a severe hydroconversion process followed by a cold hydrofinishing process to form a lubricating oil basestock.

SUMMARY

[0007] In an aspect, a method for forming a lubricant base stock is provided, the method including hydroprocessing a feedstock having a T5 boiling point greater than about 600°F (316°C) and a sulfur content of at least about 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent, the effective hydroprocessing conditions including a total pressure of less than about 1500 psig (10.3 MPag); separating the hydroprocessed effluent to form at least a gas phase effluent and a hydroprocessed liquid product effluent having a sulfur content of less than 500 wppm; dewaxing at least a first portion of the hydroprocessed liquid product effluent to form a dewaxed effluent; extracting at least a second

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portion of the hydroprocessed liquid product effluent in the presence of an extraction solvent to form a raffinate product and an extract product, the raffinate product having a sulfur content of about 300 wppm or less; and fractionating at least a portion of the raffinate product to form at least a lubricant base stock product having a viscosity index of at least about 80, and an aromatics content of about 3.0 wt% or less, or about 2.5 wt% or less, or about 2.0 wt% or less, or about 1.5 wt% or less, or about 1.0 wt% or less.

[0008] In another aspect, a method for forming a lubricant base stock is provided, the method including hydroprocessing a feedstock having a T5 boiling point greater than about 600°F (316°C) and a sulfur content of at least about 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent, the effective hydroprocessing conditions including a total pressure of less than about 1500 psig (10.3 MPag); separating the hydroprocessed effluent to form at least a gas phase effluent and a hydroprocessed liquid product effluent having a sulfur content of less than 500 wppm; exposing at least a portion of the hydroprocessed liquid product effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form a dewaxed effluent, the effective catalytic dewaxing conditions including a total pressure of about 300 psig (2.1 MPag) to about 700 psig (4.8 MPag); extracting at least a portion of the dewaxed effluent in the presence of an extraction solvent to form a raffinate product and an extract product, the raffinate product having a sulfur content of about 300 wppm or less; and fractionating at least a portion of the raffinate product to form at least a lubricant base stock product having a viscosity index of at least about 80, and an aromatics content of about 3.0 wt% or less, or about 2.5 wt% or less, or about 2.0 wt% or less, or about 1.5 wt% or less, or about 1.0 wt% or less.

[0009] In still another aspect, a method for forming a lubricant base stock is provided, the method including hydroprocessing a feedstock having a T5 boiling point greater than about 600°F (316°C) and a sulfur content of at least about 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent; exposing at least a portion of the hydroprocessing effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form a hydroprocessed, dewaxed effluent, the hydroprocessed, dewaxed effluent comprising a lubricant base oil fraction having an aromatics content of at least about 3 wt%, the lubricant base oil fraction including a first lubricant base oil portion and a second lubricant base oil portion; exposing the first lubricant base oil portion to an adsorbent to form an aromatics-depleted first lubricant base oil portion, the first lubricant base oil portion comprising about 20 wt% to about 70 wt% of the lubricant base oil fraction, an aromatics content of the aromatics-depleted first lubricant base oil portion being about 500 wppm or less; and combining the aromatics-depleted first lubricant base oil portion with the second lubricant base oil portion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. 1 schematically shows an example of a configuration suitable for processing a feedstock using both catalytic and solvent processing to form base oil products.

[0011] FIG. 2 schematically shows an example of a configuration for removing aromatics from a catalytically processed feed.

[0012] FIG. 3 shows a comparison of adsorbent selectivity for adsorption of aromatics.

[0013] FIG. 4 shows a comparison of adsorbent capacity for adsorption of aromatics.

DETAILED DESCRIPTION

[0014] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

Overview

[0015] In various aspects, methods are provided for producing lubricant base oils using a combination of catalytic and solvent processing. By using a combination of catalytic processing for feed conversion and dewaxing while using solvent processing for removal of aromatics, Group II and Group III lubricant base oils can be produced using low pressure catalytic processes. This can provide a variety of advantages. One advantage of low pressure catalytic processing is that the amount of hydrogen required for forming a lubricant base oil can be substantially reduced. In a conventional process, large hydrogen consumption and/or large hydrogen-containing treat gas rates are required in order to provide sufficient aromatic saturation. By contrast, in various aspects, after catalytic processing at low pressure of a suitable feedstock for formation of lubricant base oil(s), a solvent extraction process can be used to reduce the aromatics content to a desired level, such as less than about 3.0 wt%, or less than about 2.5 wt%, or less than about 2.0 wt%, or less than about 1.5 wt%, or less than about 1.0 wt%.

[0016] Conventionally, a feedstock for lubricant base oil production is processed either using solvent dewaxing or using catalytic dewaxing. For example,

in a lube solvent plant, a vacuum gas oil (VGO) or another suitable feed is fractionated into light neutral (LN) and heavy neutral (HN) distillates and a bottom fraction by some type of vacuum distillation. The bottoms fraction is subsequently deasphalted to recover an asphalt fraction and a deasphalted oil. The LN distillate, HN distillate, and deasphalted oil are then solvent extracted to remove the most polar molecules as an extract and corresponding raffinates of LN distillate, HN distillate, and deasphalted oil. The raffinates are then solvent dewaxed to obtain dewaxed base oils of LN distillate, HN distillate, and deasphalted oil with acceptable low temperature properties. It is beneficial to hydrofinish the lubricant basestocks either before or after the solvent dewaxing step. The resulting lubricant basestocks may contain a significant amount of aromatics (up to 50%) and high sulfur ($> 300\text{ppm}$). Thus, the typical base oils formed from solvent processing alone are Group I base stocks. As an alternative, a raffinate hydroconversion step can be performed prior to the solvent dewaxing. The hydroconversion is essentially a treatment under high H_2 pressure in presence of a metal sulfide based hydroprocessing catalyst which removes most of the sulfur and nitrogen. The amount of conversion in the hydroconversion reaction is typically tuned to obtain a predetermined increase in viscosity index and saturates. This allows the solvent dewaxed lubricant base stock products to be used as Group II or Group II+ base stocks. Optionally, the wax recovered from a solvent dewaxing unit may also be processed by catalytic dewaxing to produce Group III or Group III+ lubricant base stocks.

[0017] Current commercial methods for production of Group II and Group III base oils typically use solvent processing in only a limited manner. With the exception of solvent deasphalting at early stages of handling a crude oil fraction, processes for formation of Group II and Group III base oils typically correspond to

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catalytic processes, such as hydrotreating, hydrocracking, catalytic dewaxing, and/or aromatic saturation (sometimes referred to as hydrofinishing). Catalytic processing can be effective for producing Group II and Group III base oils having various viscosity index, viscosity, and/or pour point values. However, in order to reduce the aromatics content of the lubricant base oils to a desired level, high pressure hydroprocessing is typically required. Hydrogen is typically a limited resource in a refinery setting, so processing improvements that can allow for production of a high value product, such as a lubricant base oil, while reducing or minimizing the hydrogen consumption are highly desirable. Additionally, performing a sufficient amount of hydrocracking to reduce the aromatics content of a heavy oil fraction, such as a feed having at least 50 wt% of compounds with a boiling point of about 900°F (482°C) or more, can lead to overcracking of the heavy oil fraction.

[0018] In contrast to conventional methods, in various aspects a feedstock suitable for forming lubricant base oil products can be processed in a reaction system using catalytic processing to achieve desired levels of heteroatom removal, viscosity index improvement, and pour point reduction. A solvent extraction process can then be used to reduce the aromatics content to a desired level. For example, a vacuum gas oil or other suitable feedstock can be hydroprocessed (hydrotreated and/or hydrocracked) under sour conditions for heteroatom removal and optionally for improvement of viscosity index and then catalytically dewaxed (sweet or sour conditions) to improve cold flow properties. The hydroprocessing can be performed at a pressure of 1500 psig (10.3 MPag), while the catalytic dewaxing can be performed at a pressure of about 700 psig (4.8 MPag) or less. These pressures are substantially lower than conventional conditions for catalytic processing of a lubricant base oil. As a result, the effluent generated from the

catalytic dewaxing has a higher than expected aromatics content, such as an aromatics content of about 5 wt% to about 30 wt%. The aromatics content is then reduced to less than about 3.0 wt%, or less than about 2.5 wt%, or less than about 2.0 wt%, or less than about 1.5 wt%, or less than about 1.0 wt%, using a solvent extraction process. Optionally, the dewaxed effluent and extracted effluent can be hydrofinished in suitable manner for production of a lubricant base oil. The extract from the solvent extraction can also correspond to an upgraded product due to the hydroprocessing that occurs prior to the solvent extraction.

[0019] In some alternative aspects, instead of performing catalytic dewaxing, solvent dewaxing can be used. In such aspects, after the initial hydroprocessing, at least a portion of the hydroprocessed effluent can be solvent extracted. The raffinate from extraction can then be hydrofined followed by solvent dewaxing. Hydrofining conditions can correspond to hydrotreating conditions, hydrofinishing conditions, or a combination thereof.

[0020] In various additional or alternative aspects, methods are provided for using an adsorbent to reduce the aromatics content of a potential lubricant base oil. A feed being processed for lubricant base oil formation can end up with an excess amount of aromatics for a variety of reasons. For example, during production of a Group II base oil, a hydrotreating process may be less effective than desired, resulting in a potential base oil after hydrotreating with an aromatics content of at least about 3 wt%, or at least about 5 wt%. As another example, during catalytic processing to form a Group II base oil, the final hydrofinishing catalyst for controlling aromatics content can deactivate over time. However, it may not be desirable to stop base oil production to change out all or a portion of the catalyst. As a result, near the end of the useful processing lifetime for a hydrofinishing

catalyst, the aromatics content of a resulting Group II or Group III base oil may increase.

[0021] In order to reduce the aromatics content of a potential lubricant base oil to a desired amount, a portion of the effluent from the solvent and/or catalytic process can be exposed to an adsorbent that is suitable for adsorption of aromatics. Exposing only a portion of the effluent to the adsorbent can provide a variety of advantages. For example, since only a portion of the effluent is exposed to the adsorbent, the rate of accumulation of aromatics can be reduced, which can increase the time required between regeneration cycles for the adsorbent. Additionally, the aromatics separated from the effluent via adsorption can be captured during regeneration of the adsorbent as a separate aromatics-enriched product stream. The portion of a lubricant base oil exposed to an adsorbent can be any convenient amount, such as about 20 wt% to 100 wt% of the lubricant base oil. In some aspects, the portion of the lubricant base oil can correspond to less than the full amount of lubricant base oil, such as about 20 wt% to about 70 wt%, and/or at least about 40 wt%, and/or about 60 wt% or less.

[0022] Suitable adsorbents can include zeolite adsorbents, such as the NH_4^+ exchanged form of zeolite Beta, or Ag impregnated USY. After adsorption of a sufficient amount of aromatics, such as about 5 wt% to about 20 wt% of aromatics relative to the weight of the adsorbent, or about 5 wt% to about 15 wt%, or about 10 wt% to about 15 wt%, the adsorbent can be regenerated by exposing the adsorbent to a desorption solvent. Toluene is an example of a suitable desorption solvent. During processing of a feed, multiple adsorbent beds can be used so that some adsorbent beds are active while other beds are being regenerated.

[0023] Group I basestocks or base oils are defined as base oils with less than 90 wt% saturated molecules and/or at least 0.03 wt% sulfur content. Group I basestocks also have a viscosity index (VI) of at least 80 but less than 120. Group II basestocks or base oils contain at least 90 wt% saturated molecules and less than 0.03 wt% sulfur. Group II basestocks also have a viscosity index of at least 80 but less than 120. Group III basestocks or base oils contain at least 90 wt% saturated molecules and less than 0.03 wt% sulfur, with a viscosity index of at least 120. In addition to the above formal definitions, some Group I basestocks may be referred to as a Group I+ basestock, which corresponds to a Group I basestock with a VI value of 103 to 108. Some Group II basestocks may be referred to as a Group II+ basestock, which corresponds to a Group II basestock with a VI of at least 113. Some Group III basestocks may be referred to as a Group III+ basestock, which corresponds to a Group III basestock with a VI value of at least 140.

[0024] In a hydroprocessing reaction system, one way of characterizing a reaction stage is based on the stage being a “sweet” reaction stage or a “sour” reaction stage. In this discussion, a reaction stage where the feedstock passed into to the stage contains at least about 500 wppm of sulfur, or at least about 1000 wppm of sulfur, can be referred to as a “sour” reaction stage. Optionally, the reaction stage can be characterized based on the sulfur content of both the feedstock and any treat gas passed into the reaction stage. A sour reaction stage can be in contrast to a “sweet” reaction stage, where the sulfur content in the feedstock passed into the stage is about 500 wppm or less, or about 300 wppm or less, or about 100 wppm or less, or about 50 wppm or less, or about 15 wppm or less.

[0025] In this discussion, the severity of hydroprocessing performed on a feed can be characterized based on an amount of conversion of the feedstock. In various

aspects, the reaction conditions in the reaction system can be selected to generate a desired level of conversion of a feed. Conversion of a feed is defined in terms of conversion of molecules that boil above a temperature threshold to molecules below that threshold. The conversion temperature can be any convenient temperature. For example, for a lubricant base oil production process, a suitable conversion temperature can be from about 650°F (343°C) to about 750°F (399°C). Unless otherwise specified, the conversion temperature in this discussion is a conversion temperature of 700°F (371°C).

[0026] In some aspects, using a final solvent extraction process to achieve a desired aromatics content can allow the severity of the initial hydroprocessing stage(s) to be reduced. For example, the amount of conversion in the initial hydroprocessing stage can be about 10 wt% to less than about 30 wt% relative to a conversion temperature of 700°F (371°C). This is in contrast to a conventional lubricant production process, which can typically require a conversion amount of from about 30 wt% to about 50 wt% or more.

[0027] In the discussion below, a stage can correspond to a single reactor or a plurality of reactors. Optionally, multiple parallel reactors can be used to perform one or more of the processes, or multiple parallel reactors can be used for all processes in a stage. Each stage and/or reactor can include one or more catalyst beds containing hydroprocessing catalyst. Note that a “bed” of catalyst in the discussion below can refer to a partial physical catalyst bed. For example, a catalyst bed within a reactor could be filled partially with a hydrocracking catalyst and partially with a dewaxing catalyst. For convenience in description, even though the two catalysts may be stacked together in a single catalyst bed, the hydrocracking

catalyst and dewaxing catalyst can each be referred to conceptually as separate catalyst beds.

[0028] In the discussion herein, reference will be made to a hydroprocessing reaction system. The hydroprocessing reaction system corresponds to the one or more stages, such as two stages and/or reactors and an optional intermediate separator, that are used to expose a feed to a plurality of catalysts under hydroprocessing conditions. The plurality of catalysts can be distributed between the stages and/or reactors in any convenient manner, with some preferred methods of arranging the catalyst described herein.

[0029] In this discussion, the distillate fuel boiling range is defined as 350°F (177°C) to 700°F (371°C). Distillate fuel boiling range products can include products suitable for use as kerosene products (including jet fuel products) and diesel products, such as premium diesel or winter diesel products. In this discussion, the naphtha boiling range is defined as 36°C (97°F) to about 177°C (350°F).

Feedstocks

[0030] A wide range of petroleum and chemical feedstocks can be hydroprocessed in accordance with the disclosure. Suitable feedstocks include whole and reduced petroleum crudes, atmospheric and vacuum residua, deasphalted residua, cycle oils, FCC tower bottoms, gas oils, including vacuum gas oils and coker gas oils, light to heavy distillates including raw virgin distillates, hydrocrackates, hydrotreated oils, slack waxes, Fischer-Tropsch waxes, raffinates, and mixtures of these materials.

[0031] One way of defining a feedstock is based on the boiling range of the feed. One option for defining a boiling range is to use an initial boiling point for a feed and/or a final boiling point for a feed. Another option, which in some instances may provide a more representative description of a feed, is to characterize a feed based on the amount of the feed that boils at one or more temperatures. For example, a “T5” boiling point for a feed is defined as the temperature at which 5 wt% of the feed will boil off. Similarly, a “T95” boiling point is a temperature at 95 wt% of the feed will boil.

[0032] Typical feeds include, for example, feeds with an initial boiling point of at least about 650°F (343°C), or at least about 700°F (371°C), or at least about 750°F (399°C). Alternatively, a feed may be characterized using a T5 boiling point, such as a feed with a T5 boiling point of at least about 650°F (343°C), or at least about 700°F (371°C), or at least about 750°F (399°C). In some aspects, the final boiling point of the feed can be at least about 1100°F (593°C), such as at least about 1150°F (621°C) or at least about 1200°F (649°C). In other aspects, a feed may be used that does not include a large portion of molecules that would traditional be considered as vacuum distillation bottoms. For example, the feed may correspond to a vacuum gas oil feed that has already been separated from a traditional vacuum bottoms portion. Such feeds include, for example, feeds with a final boiling point of about 1150°F (621°C), or about 1100°F (593°C) or less, or about 1050°F (566°C) or less. Alternatively, a feed may be characterized using a T95 boiling point, such as a feed with a T95 boiling point of about 1150°F (621°C) or less, or about 1100°F (593°C) or less, or about 1050°F (566°C) or less. An example of a suitable type of feedstock is a wide cut vacuum gas oil (VGO) feed, with a T5 boiling point of at least about 700°F (371°C) and a T95 boiling point of about 1100°F or less. Optionally, the initial boiling point of such a wide cut VGO feed

can be at least about 700°F and/or the final boiling point can be at least about 1100°F. It is noted that feeds with still lower initial boiling points and/or T5 boiling points may also be suitable, so long as sufficient higher boiling material is available so that the overall nature of the process is a lubricant base oil production process and/or a fuels hydrocracking process.

[0033] The above feed description corresponds to a potential feed for producing lubricant base oils. In some aspects, methods are provided for producing both fuels and lubricants. When fuels are an additional desired product, feedstocks with lower boiling components may also be suitable. For example, a feedstock suitable for fuels production, such as a light cycle oil, can have a T5 boiling point of at least about 350°F (177°C), such as at least about 400°F (204°C). Examples of a suitable boiling range include a boiling range of from about 350°F (177°C) to about 700°F (371°C), such as from about 390°F (200°C) to about 650°F (343°C). Thus, a portion of the feed used for fuels and lubricant base oil production can include components having a boiling range from about 170°C to about 350°C. Such components can be part of an initial feed, or a first feed with a T5 boiling point of about 650°F (343°C) can be combined with a second feed, such as a light cycle oil, that includes components that boil between 200°C and 350°C.

[0034] Many typical feeds for production of lubricant base oils can have a substantial sulfur content. For example, the sulfur content of a feed prior to exposing the feed to hydroprocessing for heteroatom removal can be at least about 300 ppm by weight of sulfur, or at least about 500 wppm, or at least about 1000 wppm, or at least about 2000 wppm, or at least about 4000 wppm, or at least about 10,000 wppm, or at least about 20,000 wppm. Typical feeds can also have substantial aromatics content. Prior to exposing the feed to hydroprocessing, the

aromatics content of a feed can be at least about 10 wt%, or at least about 15 wt%, or at least about 20 wt%, or at least about 30 wt%, or at least about 40 wt%. After any catalytic processing, the aromatics content of the catalytically processed effluent can be about 5 wt% to about 30 wt% or about 5 wt% to about 25 wt%, or about 5 wt% to about 20 wt%, or about 5 wt% to about 15 wt%, or about 10 wt% to about 30 wt%, or about 10 wt% to about 25 wt%, or about 10 wt% to about 20 wt%, or about 10 wt% to about 15 wt%, or about 15 wt% to about 30 wt%, or about 15 wt% to about 25 wt%, or about 15 wt% to about 20 wt%.

[0035] In some embodiments, at least a portion of the feed can correspond to a feed derived from a biocomponent source. In this discussion, a biocomponent feedstock refers to a hydrocarbon feedstock derived from a biological raw material component, from biocomponent sources such as vegetable, animal, fish, and/or algae. Note that, for the purposes of this document, vegetable fats/oils refer generally to any plant based material, and can include fat/oils derived from a source such as plants of the genus *Jatropha*. Generally, the biocomponent sources can include vegetable fats/oils, animal fats/oils, fish oils, pyrolysis oils, and algae lipids/oils, as well as components of such materials, and in some embodiments can specifically include one or more type of lipid compounds. Lipid compounds are typically biological compounds that are insoluble in water, but soluble in nonpolar (or fat) solvents. Non-limiting examples of such solvents include alcohols, ethers, chloroform, alkyl acetates, benzene, and combinations thereof.

[0036] In some aspects, it may be desirable to fractionate a feedstock for lubricant base oil production so that different portions of the feed can be processed under different conditions. This can be one method for forming at least two lubricant base oil products from a feedstock. For example, a suitable feedstock can

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be separated to form at least a lower boiling feedstock portion, a higher boiling feedstock portion, and a bottoms portion. Such a separation can be performed, for example, using a vacuum distillation unit. One method for determining the amounts in the various portions is by selecting cut point temperatures. The cut point temperatures may vary depending on the nature of the feedstock. Generally, the cut point between the lower boiling portion and the higher boiling portion can be between about 850°F (454°C) and 950°F (510°C), such as at least about 875°F (468°C) or less than about 925°F (496°C) or less than about 900°F (482°C). The cut point between the higher boiling portion and the bottoms portion can be between about 1050°F (566°C) and about 1150°F (621°C), such as less than about 1100°F (593°C). In some alternative aspects, it may be desirable to increase the relative amount of light neutral base oils that are produced. In such aspects, the cut point between the lower boiling portion and the higher boiling portion may be higher, such as at least about 950°F (510°C), or at least about 1000°F (538°C), and less than about 1150°F (621°C), such as less than about 1100°F (593°C) or less than about 1050°F (566°C).

[0037] It is noted that the above fractionation temperatures represent the split between lighter feedstock portions, heavier feedstock portions, and a bottoms portion. If desired, additional fractions could also be formed based on additional cut points. For the purposes of the discussion herein, any such additional fractions can be processed according to boiling range. Thus, if additional fractions are formed with a T95 boiling point of less than about 850°F (454°C) to about 950°F (510°C), all such additional fractions would be processed as part of the lower boiling feedstock portion.

Hydroprocessing for Base Oil Production

[0038] After optional separation in a vacuum distillation apparatus, a feedstock for lubricant base oil production can be passed into a hydroprocessing reaction system. An initial stage of the reaction system can be used for contaminant removal to produce a hydroprocessed effluent having a sulfur content of about 100 wppm or less, or about 50 wppm or less, or about 15 wppm or less. A separation can then be performed to remove lower boiling portions of the hydroprocessed effluent. This separation can remove compounds that are gasses at standard temperature and pressure (such as H₂S, NH₃, and C₄- compounds), or the separation can remove a portion of the effluent that corresponds to naphtha and/or distillate fuel boiling range compounds. The remaining liquid portion of the effluent can then be catalytically dewaxed. Due to the separation, the catalytic dewaxing step can be performed under sweet processing conditions.

[0039] The hydroprocessing (hydrotreating and/or hydrocracking) conditions in the reaction system can also be selected to generate a desired level of conversion of a feed. Conversion of the feed can be defined in terms of conversion of molecules that boil above a temperature threshold to molecules below that threshold. The conversion temperature can be any convenient temperature, such as about 700°F (371°C). In an aspect, the amount of conversion in the stage(s) of the reaction system can be selected to enhance diesel production while achieving a substantial overall yield of fuels. The amount of conversion can correspond to the total conversion of molecules within a stage of the reaction system that is used to catalytically process the feed for lubricant base oil production. Suitable amounts of conversion of molecules boiling above 700°F to molecules boiling below 700°F include converting at least about 5 wt% of the 700°F+ portion of the feedstock in the hydroprocessing stage(s), or at least about 10 wt%, or at least about 15 wt%, or

at least about 20%, or at least about 25% of the 700°F+ portion. Additionally or alternately, the amount of conversion for the reaction system can be about 35% or less, or about 30% or less, or about 25% or less, or about 20% or less. Still larger amounts of conversion may also produce a suitable effluent for forming lubricant base oils, but such higher conversion amounts will also result in a reduced yield of lubricant base oils. Reducing the amount of conversion can increase the yield of lubricant base oils, but reducing the amount of conversion to below the ranges noted above may result in a catalytically processed effluent that is not suitable for formation of Group II or Group III lubricant base oils. In various aspects, the catalytic dewaxing stage(s) of the reaction system can convert about 1 wt% to about 10 wt% of feed to the dewaxing stage(s), such as about 1 wt% to about 5 wt%.

Hydrotreatment Conditions

[0040] Heteroatoms can be removed from a feedstock under effective hydrotreatment conditions, effective hydrocracking conditions, or a combination thereof. Hydrotreatment is typically used to reduce the sulfur, nitrogen, and aromatic content of a feed. The catalysts used for hydrotreatment can include conventional hydroprocessing catalysts, such as those that comprise at least one Group VIII non-noble metal (Columns 8 – 10 of IUPAC periodic table), preferably Fe, Co, and/or Ni, such as Co and/or Ni; and at least one Group VI metal (Column 6 of IUPAC periodic table), preferably Mo and/or W. Such hydroprocessing catalysts can comprise 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. Alternatively, the catalyst can correspond to a substantially carrier- or support-free catalyst, commonly referred to as a bulk catalyst.

[0041] For a supported hydrotreating catalyst, any convenient support material can be used. 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. Suitable aluminas are porous aluminas such as gamma or eta having average pore sizes from 50 to 200 Å, or 75 to 150 Å; a surface area from 100 to 300 m²/g, or 150 to 250 m²/g; and a pore volume of from 0.25 to 1.0 cm³/g, or 0.35 to 0.8 cm³/g. More generally, any convenient size, shape, and/or pore size distribution for a catalyst suitable for hydrotreatment of a distillate (including lubricant base oil) boiling range feed in a conventional manner may be used. It is within the scope of the present disclosure that more than one type of hydroprocessing catalyst can be used in one or multiple reaction vessels.

[0042] 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 40 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 70 wt%, preferably for supported catalysts 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. Suitable metal catalysts include cobalt/molybdenum (1-10% Co as oxide, 10-40% Mo as oxide), nickel/molybdenum (1-10% Ni as oxide, 10-40% Co as oxide), or nickel/tungsten (1-10% Ni as oxide, 10-40% W as oxide) on alumina, silica, silica-alumina, or titania.

[0043] The hydrotreatment 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

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gas, as referred to in this disclosure, 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 gasses (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 H_2S and NH_3 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, or at least about 80 vol% hydrogen, or at least about 90 vol% hydrogen.

[0044] Effective hydrotreating conditions can include temperatures of 200°C to 450°C , or 315°C to 425°C ; liquid hourly space velocities (LHSV) of 0.1 hr^{-1} to 10 hr^{-1} ; and hydrogen treat rates of 200 scf/B ($35.6\text{ m}^3/\text{m}^3$) to 10,000 scf/B ($1781\text{ m}^3/\text{m}^3$), or 500 ($89\text{ m}^3/\text{m}^3$) to 5,000 scf/B ($890.5\text{ m}^3/\text{m}^3$). With regard to pressure, the hydrotreating can be performed at a pressure of about 300 psig (2.1 MPag) to about 1500 psig (10.4 MPag), or about 750 psig (5.2 MPag) to about 1500 psig (10.4 MPag), or about 1000 psig (6.9 MPag) to about 1500 psig (10.4 MPag), or about 1200 psig (8.3 MPag) to about 1500 psig (10.4 MPag).

Hydrocracking Conditions

[0045] In addition to or as an alternative to hydrotreating, hydrocracking can be used to hydroprocess a feed for heteroatom removal. Hydrocracking catalysts typically contain sulfided base metals on acidic supports, such as amorphous silica alumina, acidic zeolites such as USY, or acidified alumina. Often these acidic supports are mixed or bound with other metal oxides such as alumina, titania or silica. Examples of suitable acidic supports include acidic molecular sieves, such as

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zeolites or silicoaluminophosphates. One example of suitable zeolite is USY, such as a USY zeolite with cell size of 24.25 Angstroms or less. Additionally or alternately, the catalyst can be a low acidity molecular sieve, such as a USY zeolite with a Si to Al ratio of at least about 20, and preferably at least about 40 or 50. Zeolite Beta is another example of a potentially suitable hydrocracking catalyst. Non-limiting examples of metals for hydrocracking catalysts include metals or combinations of metals that include at least one Group VIII metal, such as nickel, nickel-cobalt-molybdenum, cobalt-molybdenum, nickel-tungsten, nickel-molybdenum, and/or nickel-molybdenum-tungsten. Support materials which may be used for can comprise a refractory oxide material such as alumina, silica, alumina-silica, kieselguhr, diatomaceous earth, magnesia, zirconia, or combinations thereof, with alumina, silica, alumina-silica being the most common (and preferred, in one embodiment). In some aspects, a hydrotreating catalyst as described above can be exposed to a feed under effective hydrocracking conditions to perform hydrocracking on a feed.

[0046] In various aspects, effective hydrocracking conditions for a hydrocracking process can include temperatures of about 550°F (288°C) to about 840°F (449°C), liquid hourly space velocities of from 0.05 h⁻¹ to 10 h⁻¹, and hydrogen treat gas rates of from 35.6 m³/m³ to 1781 m³/m³ (200 SCF/B to 10,000 SCF/B). In other embodiments, the conditions can include temperatures in the range of about 600°F (343°C) to about 815°F (435°C), liquid hourly space velocities of from 0.05 h⁻¹ to 10 h⁻¹, and hydrogen treat gas rates of from about 213 m³/m³ to about 1068 m³/m³ (1200 SCF/B to 6000 SCF/B). With regard to pressure, the hydrocracking can be performed at a pressure of about 300 psig (2.1 MPag) to about 1500 psig (10.4 MPag), or about 750 psig (5.2 MPag) to about 1500 psig

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(10.4 MPag), or about 1000 psig (6.9 MPag) to about 1500 psig (10.4 MPag), or about 1200 psig (8.3 MPag) to about 1500 psig (10.4 MPag).

Catalytic Dewaxing Process

[0047] After hydrotreating and/or hydrocracking for heteroatom removal, at least a (liquid) portion of the resulting effluent can be catalytically dewaxed for improvement of pour point and/or other cold flow properties. Suitable dewaxing catalysts can include molecular sieves such as crystalline aluminosilicates (zeolites). In some aspects, any conventional dewaxing catalyst can be used. In other aspects, the molecular sieve can comprise, consist essentially of, or be ZSM-5, ZSM-22, ZSM-23, ZSM-35, ZSM-48, zeolite Beta, or a combination thereof, for example ZSM-23 and/or ZSM-48, or ZSM-48 and/or zeolite Beta. Optionally but preferably, molecular sieves that are selective for dewaxing by isomerization as opposed to cracking can be used, such as ZSM-48, zeolite Beta, ZSM-23, or a combination thereof. Additionally or alternately, the molecular sieve can comprise, consist essentially of, or be a 10-member ring 1-D molecular sieve. Examples include EU-1, ZSM-35 (or ferrierite), ZSM-11, ZSM-57, NU-87, SAPO-11, ZSM-48, ZSM-23, and ZSM-22. Preferred materials are EU-2, EU-11, ZBM-30, ZSM-48, or ZSM-23. ZSM-48 is most preferred. Note that a zeolite having the ZSM-23 structure with a silica to alumina ratio of from about 20:1 to about 40:1 can sometimes be referred to as SSZ-32. Other molecular sieves that are isostructural with the above materials include Theta-1, NU-10, EU-13, KZ-1, and NU-23. Optionally but preferably, the dewaxing catalyst can include a binder for the molecular sieve, such as alumina, titania, silica, silica-alumina, zirconia, or a combination thereof, for example alumina and/or titania or silica and/or zirconia and/or titania.

[0048] Preferably, the dewaxing catalysts used in processes according to the disclosure are catalysts with a low ratio of silica to alumina. For example, for ZSM-48, the ratio of silica to alumina in the zeolite can be less than about 200:1, such as less than about 110:1, or less than about 100:1, or less than about 90:1, or less than about 75:1. In various embodiments, the ratio of silica to alumina can be from 50:1 to 200:1, such as 60:1 to 160:1, or 70:1 to 100:1.

[0049] In various embodiments, the catalysts according to the disclosure further include a metal hydrogenation component. The metal hydrogenation component is typically a Group VI and/or a Group VIII metal. Preferably, the metal hydrogenation component is a Group VIII noble metal. Preferably, the metal hydrogenation component is Pt, Pd, or a mixture thereof. In an alternative preferred embodiment, the metal hydrogenation component can be a combination of a non-noble Group VIII metal with a Group VI metal. Suitable combinations can include Ni, Co, or Fe with Mo or W, preferably Ni with Mo or W.

[0050] The metal hydrogenation component may be added to the catalyst in any convenient manner. One technique for adding the metal hydrogenation component is by incipient wetness. For example, after combining a zeolite and a binder, the combined zeolite and binder can be extruded into catalyst particles. These catalyst particles can then be exposed to a solution containing a suitable metal precursor. Alternatively, metal can be added to the catalyst by ion exchange, where a metal precursor is added to a mixture of zeolite (or zeolite and binder) prior to extrusion.

[0051] The amount of metal in the catalyst can be at least 0.1 wt% based on catalyst, or at least 0.15 wt%, or at least 0.2 wt%, or at least 0.25 wt%, or at least

0.3 wt%, or at least 0.5 wt% based on catalyst. The amount of metal in the catalyst can be 20 wt% or less based on catalyst, or 10 wt% or less, or 5 wt% or less, or 2.5 wt% or less, or 1 wt% or less. For embodiments where the metal is Pt, Pd, another Group VIII noble metal, or a combination thereof, the amount of metal can be from 0.1 to 5 wt%, preferably from 0.1 to 2 wt%, or 0.25 to 1.8 wt%, or 0.4 to 1.5 wt%. For embodiments where the metal is a combination of a non-noble Group VIII metal with a Group VI metal, the combined amount of metal can be from 0.5 wt% to 20 wt%, or 1 wt% to 15 wt%, or 2.5 wt% to 10 wt%.

[0052] Process conditions in a catalytic dewaxing zone can include a temperature of from 200 to 450°C, preferably 270 to 400°C, an LHSV from about 0.2 h⁻¹ to about 10 h⁻¹, such as from about 0.5 h⁻¹ to about 5 h⁻¹, and a treat gas rate of from 35.6 m³/m³ (200 SCF/B) to 1781 m³/m³ (10,000 scf/B), preferably 178 m³/m³ (1000 SCF/B) to 890.6 m³/m³ (5000 SCF/B). With regard to pressure, the dewaxing can be performed at a pressure of about 300 psig (2.1 MPag) to about 700 psig (4.8 MPag), or about 300 psig (2.1 MPag) to about 600 psig (4.2 MPag), or about 300 psig (2.1 MPag) to about 500 psig (3.5 MPag), or about 400 psig (2.8 MPag) to about 700 psig (4.8 MPag), or about 400 psig (2.8 MPag) to about 600 psig (4.2 MPag), or about 400 psig (2.8 MPag) to about 500 psig (3.5 MPag), or about 500 psig (3.5 MPag) to about 700 psig (4.8 MPag).

Hydrofinishing and/or Aromatic Saturation Process

[0053] In some optional aspects, a hydrofinishing and/or aromatic saturation stage can also be provided. If a solvent extraction stage is present for aromatics removal, then typically a hydrofinishing stage will not be included. However, a hydrofinishing stage may be desirable if the final aromatics removal step is via adsorption rather than by solvent extraction.

[0054] Hydrofinishing and/or aromatic saturation catalysts can include catalysts containing Group VI metals, Group VIII metals, and mixtures thereof. In an embodiment, preferred metals include at least one metal sulfide having a strong hydrogenation function. In another embodiment, the hydrofinishing catalyst can include a Group VIII noble metal, such as Pt, Pd, or a combination thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is about 30 wt. % or greater based on catalyst. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. The preferred hydrofinishing catalysts for aromatic saturation will comprise at least one metal having relatively strong hydrogenation function on a porous support. Typical support materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina. The support materials may also be modified, such as by halogenation, or in particular fluorination. The metal content of the catalyst is often as high as about 20 weight percent for non-noble metals. In an embodiment, a preferred hydrofinishing catalyst can include a material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica content. Examples include MCM-41, MCM-48 and MCM-50. A preferred member of this class is MCM-41. If separate catalysts are used for aromatic saturation and hydrofinishing, an aromatic saturation catalyst can be selected based on activity and/or selectivity for aromatic saturation, while a hydrofinishing catalyst can be selected based on activity for improving product specifications, such as product color and polynuclear aromatic reduction.

[0055] Hydrofinishing conditions can include temperatures from about 125°C to about 425°C, preferably about 180°C to about 280°C, a hydrogen partial pressure from about 500 psig (3.4 MPa) to about 3000 psig (20.7 MPa), preferably about

1500 psig (10.3 MPa) to about 2500 psig (17.2 MPa), and liquid hourly space velocity from about 0.1 hr^{-1} to about 5 hr^{-1} LHSV, preferably about 0.5 hr^{-1} to about 1.5 hr^{-1} . Additionally, a hydrogen treat gas rate of from $35.6 \text{ m}^3/\text{m}^3$ to $1781 \text{ m}^3/\text{m}^3$ (200 SCF/B to 10,000 SCF/B) can be used.

Solvent Extraction for Aromatics Removal

[0056] Solvent extraction can be used to reduce the aromatics content and/or the amount of polar molecules in the hydroprocessed, dewaxed effluent. The solvent extraction process selectively dissolves aromatic components to form an aromatics-rich extract phase while leaving the more paraffinic components in an aromatics-poor raffinate phase. Naphthenes are distributed between the extract and raffinate phases. Typical solvents for solvent extraction include phenol, furfural and N-methyl pyrrolidone. More generally, any convenient solvent for removing aromatics to about 2.5 wt% or less, or about 1.5 wt% or less, or about 1.0 wt% or less, can be used. However, use of those solvents most selective for removing aromatics, such as SO_2 , sulfolane, and DMSO, can maximize both yield of the raffinate and concentration of aromatics in the extract phase. Such selective solvents, by accentuating the difference in density between the dispersed and continuous phases, tend to overcome low rates in the coalescence step of the extraction process. By controlling the solvent to oil ratio, extraction temperature, content of water or other solvency modifier, temperature gradient in the liquid-liquid treater tower, and method of contacting hydroprocessed, dewaxed effluent to be extracted with solvent, one can further control the degree of separation between the extract and raffinate phases. Any convenient type of liquid-liquid extractor can be used, such as a counter-current liquid-liquid extractor.

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[0057] In various aspects, a suitable extraction solvent can have one or more of the following characteristics, such as two or more, or three or more, or four or more, or all of the characteristics. One characteristic can be a high polarity or high dipole moment. A solvent with a high polarity can often correspond to a solvent with a high boiling point and/or a high dipole moment. Another characteristic can be thermal and/or chemical stability under the solvent extraction conditions, which can involve elevated temperatures. Still another characteristic can be suitable miscibility with water, with organic solvents, or a combination thereof. Yet another characteristic can be a solvent which presents a reduced or minimized hazard from a fire and/or toxicological standpoint. In other words, the solvent can have properties such as a high flash point temperature (thereby reducing or minimizing fire hazard) or a low corrosiveness (thereby reducing or minimizing toxicological hazard). Still another desirable solvent characteristic can be to have a solvent that is substantially free of contaminants, such as a solvent with a purity of at least about 95 vol%, or at least about 99 vol%.

[0058] Examples of solvents that correspond to one or more of the above characteristics can include, but are not limited to, methyl pyrrolidone (NMP), furfural, phenol, SO₂, sulfolane, dimethylsulfoxide, or combinations thereof. In some aspects, a solvent can further contain a solvency modifier, such as water.

Example of Configuration for Integrated Reaction System

[0059] FIG. 1 shows a schematic example of configuration for forming lubricant base oils using both catalytic processing and solvent processing. In the configuration shown in FIG. 1, a feedstock for lubricant base oil production 105 is introduced into a vacuum distillation tower 110. The vacuum distillation tower 110 fractionates the feedstock 105 into at least a portion 115 suitable for further

processing to form a lubricant base oil. The feedstock portion 115 is then hydroprocessed 120 (i.e., hydrotreated and/or hydrocracked) to form a hydroprocessed effluent 125. The hydroprocessed effluent 125 can be separated (not shown) to remove at least gas phase heteroatom contaminants generated during hydroprocessing, such as H_2S and NH_3 . A remaining portion of the hydroprocessed effluent 125, such as a liquid portion, can then be catalytically dewaxed 130 to form a hydroprocessed, dewaxed effluent 135. The hydroprocessed, dewaxed effluent 135 can then be solvent extracted 140. This results in an aromatics-rich extract 148 and a raffinate 145 with reduced aromatics content. The raffinate 145 can have an aromatics content of less than about 2.5 wt%, or less than about 1.5 wt%, or less than about 1.0 wt%, making the raffinate suitable for use as a Group II or Group III lubricant base oil, optionally after further hydrofinishing. The aromatics-rich extract 148 represents a high quality extract product based on the low sulfur content. Additionally, it is believed that the extract 148 can have a narrower distribution of carbon atoms per molecule and be more stable to oxidative and thermal degradation than a typical extract derived from solvent processing to form a Group I base oil.

[0060] It is noted that after hydroprocessing, the order of performing additional processes on the hydroprocessed effluent 125 can be any one of a variety of convenient orderings. For example, the configuration in FIG. 1 shows a liquid portion of hydroprocessed effluent 125 being catalytically dewaxed 130. This produces a hydroprocessed, dewaxed effluent 135 which is then solvent extracted 140. As an alternative (not shown), the liquid portion of the hydroprocessed effluent 125 can be solvent extracted 140 to produce an aromatics-rich extract and a raffinate with a reduced aromatics content. The hydroprocessed raffinate can then be catalytically dewaxed to produce a dewaxed effluent that is suitable for use as a

Group II or Group III lubricant base oil, optionally after further hydrofinishing. The aromatics-rich extract generated in this alternative configuration can have properties similar to those described above for aromatics-rich extract 148 in the configuration shown in FIG. 1.

Example 1 – Solvent Extraction of a Catalytically Processed Lubricant Base Oil Feed

[0061] In the following example, a solvent extraction process was modeled for an example of a lubricant base oil feed. The modeled feed corresponded to an output stream from a hydrocracking process. The feed contained 24 % aromatics and had a density @ 15 °C of 0.8895 g/cc. The D2887 boiling points of the feed were between 340°C (IBP) to 600 °C (FBP). The modeled feed did not include sulfur or nitrogen.

[0062] An empirical-based model was then used to determine the output streams from performing an aromatic extraction process on the modeled feed under various extraction conditions. In the modeled extraction, an extractor was used that had 5 to 10 theoretical stages. In the modeled extraction, the dosage solvent was between 300 to 500 vol% of the feed, the water in the solvent was between 0.5 to 1.5 wt%, the temperature gradient was between 5 to 10 °C, and the bottom temperature was between 75 to 90 °C. The extraction was based on use of n-methyl pyrrolidone (NMP) as the solvent. The modeled results showed an aromatic content in the raffinate of between ~ 0.5 % to 1.7 % depending on the conditions.

Example 2 – Comparison with Conventional Catalytic Processing

[0063] The following example provides a qualitative yield and product comparison between a conventional configuration and a process for combined catalytic and solvent processing.

[0064] For a typical commercial Group II lubricant base oil production process, a hydrocracking unit can be operated between 2000 psig and 3000 psig pressure. This typically results in conversion of around 50 wt% of the feedstock relative to a 700°F conversion temperature. The hydrocracked feed can then be dewaxed in the presence of a dewaxing catalyst. Some typical Group II lubricant base oil production process can have about 5 wt% conversion in the catalytic dewaxing process. As an example, a typical expected lube production yield for such a conventional configuration can be about 47.5 vol% based on the volume of feed passed into the hydrocracking unit.

[0065] In some aspects, a hydrocracking and/or hydrotreating process can be used to hydroprocess a feed for lubricant base oil production to reduce the sulfur and nitrogen contents of the feed. The hydrocracking and/or hydrotreating process can also provide some increase in viscosity index for the eventual lubricant base oil process. However, because solvent extraction will be used for aromatics reduction, the conversion in the hydrocracking and/or hydrotreating stage can be lower than a conventional process. For example, the conversion in the hydroprocessing stage relative to a conversion temperature of 700°F can be about 30 wt% or less. The hydroprocessed effluent (or at least a portion of the effluent) can then be catalytically dewaxed. This can result in about 5 wt% conversion of the hydroprocessed effluent, which is similar to the conversion in the dewaxing stage of a conventional process. The hydroprocessed, dewaxed effluent can then be solvent

extracted to produce an aromatics-rich extract and a raffinate with a reduced aromatics content of about 2.5 wt% or less, or about 1.5 wt% or less, or about 1.0 wt% or less. The extraction unit can also improve the stability of the lubricant base oil product by removing polynuclear aromatics (PNAs). The total lube production for this configuration can be about 33 vol% relative to the feed to the hydroprocessing stage. However, the aromatics-rich extract stream produced in this configuration can also have a volume of about 33 vol% relative to the feed to the hydroprocessing stage. The aromatics-rich extract stream can be a premium stream since it will have low sulfur and nitrogen content and less aromatic than traditional extract streams formed during processing of a Group I lubricant base oil. In addition, this extract will be more stable and have a more narrow carbon distribution composition than traditional extracts of Group I lube production.

[0066] In an alternative aspect where the hydroprocessing stage corresponds to a hydrotreating stage, the conversion can be about 15 wt% or less, or about 10 wt% or less. Use of this type of alternative can be dependent on the nature of the initial feedstock available in a refinery. In this type of alternative, assuming a 50% efficiency in the solvent extraction unit(s), the overall yield can be about 43 vol% of Group II quality lubricant base oil, with a similar amount of premium aromatics-rich extract.

Example 3 - Adsorbents for Aromatics Removal

[0067] In some alternative aspects, methods are also provided for using an adsorbent to remove aromatics from a catalytically processed lubricant base oil product while also generating an aromatics-rich side product. In such aspects, a portion of a lubricant base oil product can be passed through an adsorbent to remove aromatics. The aromatics-depleted portion can then be recombined with the

remaining portion so that the overall product has a desired aromatics content. As an example, a lubricant base oil production process may generate 35 kilobarrels per day (kbd) of lubricant base oil. A portion of this production, such as 20 kbd, can be passed through the adsorbent. The adsorbent can be effective for reducing the aromatics concentration of the 20 kbd portion to a low level, such as less than about 500 wppm, or less than about 100 wppm. The aromatics-lean portion of the lubricant base oil can then be recombined with the remaining 15 kbd of the lubricant base oil. If the original aromatics content was, for example, about 7 wt%, the final lubricant base oil can have an aromatics content of about 3 wt%.

[0068] An advantage of the adsorbent process is that the adsorbent can be used as needed. For example, at the beginning of a processing run, the aromatics content of the lubricant base oil may be within a desired specification. As one or more catalysts deactivate, the aromatics content may increase. The adsorbent can then be used on a portion of the lubricant base oil product to maintain a desired specification.

[0069] After a period of adsorption, the adsorbent may reach a maximum desired loading of aromatics. This can correspond to, for example, about 10 wt% to about 20 wt% of aromatics relative to the weight of the adsorbent. The adsorbent vessel can then be taken off-line to allow for regeneration. The regeneration can be performed by passing a desorption solvent through the adsorbent, such as toluene. The aromatics concentrate produced during the desorption cycle can be sent to an extraction unit as feed to recover all the remaining paraffinic molecules or also as feed to Treated Distillate Aromatic Extract for the tire or asphalt industry or used as a solvency additive.

[0070] FIG. 2 schematically shows a configuration for using an adsorbent as part of a process for making a lubricant base oil. In FIG. 2, a portion of a lubricant base oil product 205 is passed into an adsorbent vessel. In the configuration shown in FIG. 2, either adsorbent vessel 240 or 241 can be in use for adsorption at any given time. During adsorption from a lubricant base oil, passing the portion of lubricant base oil product 205 through the adsorbent vessel (such as adsorbent vessel 240) produces an aromatics-lean product 215. The aromatics-lean product 215 can then be combined with the remaining portion of the lubricant base oil (not shown).

[0071] While an adsorbent vessel is not in use for adsorption, such as adsorbent vessel 241, at least a portion of the time can be used for regenerating the adsorbent vessel. In the configuration shown in FIG. 2, during a regeneration cycle, a fresh stream of desorption solvent 222 can be passed into adsorbent vessel 241. This results in desorption of aromatics from the adsorbent in vessel 241 to form an aromatics extract stream 245. A surge tank 250 can be used to control the flow of aromatics extract stream 245 to fractionator or stripper 260. The fractionator 260 can be used to separate the aromatics extract from the desorption solvent, resulting in formation of an aromatic concentration stream 265 and a recycled desorption solvent stream 262.

[0072] The adsorption methods described herein can generally be used with any lubricant base oil product where a partial reduction of aromatics content is desired. The adsorbent can be any adsorbent that is selective for adsorption of aromatics relative to paraffins and naphthenes. Molecular sieves can be suitable adsorbents, such as zeolite H-Beta and Ag/USY or other zeolites (5A, 13X, MCM-22, MCM-68 and ZSM-5). The adsorbents could also include active

carbons, mesoporous silica, M41S family of materials, sulfonated polymers such as Amberlyst acid ion exchanged resin, Nafion, It is believe that adsorption primarily occurs on the surface and temperature may influence the diffusion of large aromatic molecules through viscous liquids. Key parameters of desirable adsorbent are related to acidity, pore size and mesoporous / macroporous nature. A metal cation modified adsorbent may also impact on capacity/separation factor of aromatic adsorption. Some suitable metals cations can include, but are not limited to, Ag⁺, Na⁺, Ca²⁺, and Cu⁺. In this discussion, a metal cation can be identified by simply referring to a cation of the corresponding metal, such as by referring to a cation of Ag, Na, Ca, or Cu, without explicitly reciting an oxidation state.

[0073] The adsorption and desorption processes can be performed at temperatures from about 80°C to about 300°C. The amount of desorption solvent can be about 1 g of solvent per g of adsorbent used. As a comparison, each kg of adsorbent is suitable for treating about 2000 barrels of lubricant base oil.

Example 4 - Adsorption of a Catalytically Processed Lubricant Base Oil Feed

[0074] In the following example, an adsorption process was applied for making a lubricant base oil feed with improved saturate content. The hydroprocessed and dewaxed feed corresponded to an output stream from a hydrocracking/dewaxing process. These feed properties are summarized in the table below.

Table 1. Properties of a lube basestock to be treated via adsorption:

Property(Test Method)	Result	Result
KV100, KV40 (D445)	5.28 cSt, 29.26 cSt	5.3 cSt, 29.1 cSt
Density (D4052)	0.8527 g/mL	0.854 g/mL
Flashpoint (D92)	226°C	218°C
Total Aromatics (M1514) (mmol/kg)	63.12	86
1+ Ring, mmol/kg	53.8	73.3
2+ Ring, mmol/kg	6.96	9.8
3+ Ring, mmol/kg	0.57	1.1
4+ Ring, mmol/kg	1.99	2.9

[0075] As the first pass of adsorbent screening, 3 g of feed was charged into a batch multi-wells unit with varied adsorbent loadings (100 mg to 800 mg). Various absorbents were tested with 24 hours run-length at 30°C. The liquid product was recovered and submitted for aromatics measurement by UV-Vis. In adsorption data analysis, lube basestock feed was taken as a binary mixture containing all aromatic molecules lumped together as a single entity and non-aromatic molecules being the other component. The capacity and selectivity of adsorbent were calculated using direct experimental measurements of total moles & composition of liquid before and after contact with adsorbent, and adsorbent loading. These two adsorption parameters are defined as the adsorption separation factor (S12) and the adsorbent capacity (g aromatic adsorbed/100 g Adsorbent). Over a group of adsorbents screened using the static experiments, H-Beta and 5 wt% Ag/USY showed preferential adsorption of aromatic molecules over saturates. As shown is FIG. 3, maximum average separation factor S12 was significant for H-Beta and 5 wt%

Ag/USY. For H-Beta and 5 wt% Ag/USY, the S12 for 1-ring aromatic molecules over saturates was observed to be ~ 9-10. The adsorbent capacity for H-Beta and 5 wt% Ag/USY was also determined to be ~ 4, as illustrated in FIG. 4.

[0076] Any convenient cycle can be used for adsorption and/or regeneration. For example, adsorption of aromatics can be performed by filling the adsorbent vessel, holding the base oil in the vessel for a period of time, emptying the vessel, filling the vessel with the desorption solvent, and then holding the desorption solvent for a period of time. Using this type of schedule, the empty / fill portion of the schedule can correspond to about 30 minutes, while the holding time (for lubricant base oil or for desorption solvent) can be about 2 hours. The adsorption and/or desorption processes can be performed at isothermal (approximately constant temperature) or non-isothermal conditions.

Additional Embodiments

[0077] Embodiment 1. A method for forming a lubricant base stock, comprising: hydroprocessing a feedstock having a T5 boiling point greater than about 600°F (316°C) and a sulfur content of at least about 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent, the effective hydroprocessing conditions including a total pressure of less than about 1500 psig (10.3 MPag); separating the hydroprocessed effluent to form at least a gas phase effluent and a hydroprocessed liquid product effluent having a sulfur content of less than 500 wppm; dewaxing at least a first portion of the hydroprocessed liquid product effluent to form a dewaxed effluent; extracting at least a second portion of the hydroprocessed liquid product effluent in the presence of an extraction solvent to form a raffinate product and an extract product, the raffinate product having a sulfur content of about 300 wppm or less; and fractionating at

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least a portion of the raffinate product to form at least a lubricant base stock product having a viscosity index of at least about 80, and an aromatics content of about 3.0 wt% or less, or about 2.5 wt% or less, or about 2.0 wt% or less, or about 1.5 wt% or less, or about 1.0 wt% or less.

[0078] Embodiment 2. The method of Embodiment 1, further comprising hydrofining at least a portion of the raffinate product under effective hydrofining conditions to form a hydrofined raffinate, wherein dewaxing at least a first portion of the hydroprocessed liquid product effluent comprises solvent dewaxing at least a portion of the hydrofined raffinate.

[0079] Embodiment 3. The method of Embodiment 1, wherein dewaxing at least a first portion of the hydroprocessed liquid product effluent comprises exposing the at least a first portion of the hydroprocessed liquid product effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form the dewaxed effluent, the effective catalytic dewaxing conditions including a total pressure of about 300 psig (2.1 MPag) to about 700 psig (4.8 MPag), wherein extracting at least a second portion of the hydroprocessed liquid product effluent comprises extracting at least a portion of the dewaxed effluent.

[0080] Embodiment 4. A method for forming a lubricant base stock, comprising: hydroprocessing a feedstock having a T5 boiling point greater than about 600°F (316°C) and a sulfur content of at least about 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent, the effective hydroprocessing conditions including a total pressure of less than about 1500 psig (10.3 MPag); separating the hydroprocessed effluent to form at least a gas phase effluent and a hydroprocessed liquid product effluent having a sulfur content

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of less than 500 wppm; exposing at least a portion of the hydroprocessed liquid product effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form a dewaxed effluent, the effective catalytic dewaxing conditions including a total pressure of about 300 psig (2.1 MPag) to about 700 psig (4.8 MPag); extracting at least a portion of the dewaxed effluent in the presence of an extraction solvent to form a raffinate product and an extract product, the raffinate product having a sulfur content of about 300 wppm or less; and fractionating at least a portion of the raffinate product to form at least a lubricant base stock product having a viscosity index of at least about 80, and an aromatics content of about 3.0 wt% or less, or about 2.5 wt% or less, or about 2.0 wt% or less, or about 1.5 wt% or less, or about 1.0 wt% or less.

[0081] Embodiment 5. The method of Embodiments 3 or 4, wherein the effective dewaxing conditions comprise a total pressure of about 300 psig (2.1 MPag) to about 600 psig (4.2 MPag), or about 300 psig (2.1 MPag) to about 500 psig (3.5 MPag), or about 400 psig (2.8 MPag) to about 700 psig (4.8 MPag), or about 400 psig (2.8 MPag) to about 600 psig (4.2 MPag), or about 400 psig (2.8 MPag) to about 500 psig (3.5 MPag), or about 500 psig (3.5 MPag) to about 700 psig (4.8 MPag), the effective dewaxing conditions optionally being effective for conversion of about 1 wt% to about 10 wt% of the at least a portion of the hydroprocessed liquid product effluent, or about 1 wt% to about 5 wt%.

[0082] Embodiment 6. The method of any of Embodiments 3 to 5, wherein the dewaxed effluent has an aromatics content of about 5 wt% to about 30 wt% or about 5 wt% to about 25 wt%, or about 5 wt% to about 20 wt%, or about 5 wt% to about 15 wt%, or about 10 wt% to about 30 wt%, or about 10 wt% to about 25 wt%, or about 10 wt% to about 20 wt%, or about 10 wt% to about 15 wt%, or about 15

wt% to about 30 wt%, or about 15 wt% to about 25 wt%, or about 15 wt% to about 20 wt%.

[0083] Embodiment 7. The method of any of the above embodiments, further comprising hydrofinishing at least a portion of the dewaxed effluent under effective hydrofinishing conditions.

[0084] Embodiment 8. The method of any of the above embodiments, wherein fractionating the at least a portion of the raffinate product further comprises forming a distillate boiling range product.

[0085] Embodiment 9. The method of any of the above embodiments, further comprising separating the dewaxed effluent to form a fraction having a T5 boiling point of at least about 500°F and at least one fuel product, the at least one fuel product being a naphtha boiling range product or a distillate fuel boiling range product, wherein extracting at least a portion of the dewaxed effluent comprises extracting at least a portion of the fraction having a T5 boiling point of at least about 500°F (260°C).

[0086] Embodiment 10. The method of any of the above embodiments, wherein separating the hydroprocessed effluent further comprises forming at least one fuel product, the at least one fuel product being a naphtha boiling range product or a distillate fuel boiling range product.

[0087] Embodiment 11. The method of any of the above embodiments wherein the effective hydroprocessing conditions comprise a total pressure of about 300 psig (2.1 MPag) to about 1500 psig (10.4 MPag), or about 750 psig (5.2 MPag)

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to about 1500 psig (10.4 MPag), or about 1000 psig (6.9 MPag) to about 1500 psig (10.4 MPag), or about 1200 psig (8.3 MPag) to about 1500 psig (10.4 MPag), the hydroprocessed liquid product effluent optionally having a sulfur content of about 100 wppm or less, or about 50 wppm or less, or about 15 wppm or less.

[0088] Embodiment 12. The method of any of the above embodiments, wherein the effective hydroprocessing conditions comprise effective hydrotreating conditions, effective hydrocracking conditions, or a combination thereof, the effective hydroprocessing conditions optionally being effective for conversion of about 5 wt% to about 30 wt% of the feedstock having a T5 boiling point greater than about 600°F (316°C) relative to a conversion temperature of about 700°F (371°C), or about 10 wt% to about 25 wt%, or about 10 wt% to about 20 wt%, or about 5 wt% to about 15 wt%, or about 5 wt% to about 10 wt%.

[0089] Embodiment 13. The method of any of the above embodiments, wherein the extraction solvent comprises methyl pyrrolidone (NMP), furfural, phenol, SO₂, sulfolane, dimethylsulfoxide, or a combination thereof.

[0090] Embodiment 14. A method for forming a lubricant base stock, comprising: hydroprocessing a feedstock having a T5 boiling point greater than about 600°F (316°C) and a sulfur content of at least about 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent; exposing at least a portion of the hydroprocessing effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form a hydroprocessed, dewaxed effluent, the hydroprocessed, dewaxed effluent comprising a lubricant base oil fraction having an aromatics content of at least about 3 wt%, the lubricant base oil fraction including a first lubricant base oil portion and a second lubricant base oil

portion; exposing the first lubricant base oil portion to an adsorbent to form an aromatics-depleted first lubricant base oil portion, the first lubricant base oil portion comprising about 20 wt% to about 70 wt% of the lubricant base oil fraction, an aromatics content of the aromatics-depleted first lubricant base oil portion being about 500 wppm or less; and combining the aromatics-depleted first lubricant base oil portion with the second lubricant base oil portion.

[0091] Embodiment 15. The method of Embodiment 14, wherein the adsorbent comprises one or more of zeolites, active carbon, mesoporous silica, materials corresponding to the M41S family of materials, and sulfonated polymers, the adsorbent optionally comprising one or more of zeolite Beta, USY, zeolite 5A, zeolite 13X, MCM-22, MCM-68, ZSM-5, MCM-41, Amberlyst acid ion exchanged resin and Nafion, the adsorbent optionally further comprising metal cations, the metal cations optionally comprising cations of Ag, Na, Ca, Cu, or a combination thereof.

[0092] Embodiment 16. The method of Embodiments 14 or 15, further comprising exposing the adsorbent to a desorption solvent to form an aromatics extract fraction.

[0093] Embodiment 17. The method of any of Embodiments 14 to 16, further comprising hydrofinishing at least a portion of the hydroprocessed, dewaxed effluent to form a hydrofinished effluent, the hydrofinished effluent comprising the lubricant base oil fraction.

[0094] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the

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illustrative embodiments of the disclosure have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present disclosure, including all features which would be treated as equivalents thereof by those skilled in the art to which the disclosure pertains.

[0095] The present disclosure has been described above with reference to numerous embodiments and specific examples. Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious variations are within the full intended scope of the appended claims.

CLAIMS:

1. A method for forming a lubricant base stock, comprising:

hydroprocessing a feedstock having a T5 boiling point greater than 600°F (316°C) and a sulfur content of at least 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent, the effective hydroprocessing conditions including a total pressure of less than 1500 psig (10.3 MPag);

separating the hydroprocessed effluent to form at least a gas phase effluent and a hydroprocessed liquid product effluent having a sulfur content of less than 500 wppm;

dewaxing at least a first portion of the hydroprocessed liquid product effluent to form a dewaxed effluent;

extracting at least a second portion of the hydroprocessed liquid product effluent in the presence of an extraction solvent to form a raffinate product and an extract product, the raffinate product having a sulfur content of 300 wppm or less; and

fractionating at least a portion of the raffinate product to form at least a lubricant base stock product having a viscosity index of at least 80, and an aromatics content of 2.5 wt% or less.

2. The method of claim 1, wherein dewaxing at least a first portion of the hydroprocessed liquid product effluent comprises exposing the at least a first portion of the hydroprocessed liquid product effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form the dewaxed effluent, the effective catalytic dewaxing conditions including a total pressure of 300 psig (2.1 MPag) to 700 psig (4.8 MPag), wherein extracting at least a second portion of the

hydroprocessed liquid product effluent comprises extracting at least a portion of the dewaxed effluent.

3. The method of claim 2, wherein the effective dewaxing conditions comprise a total pressure of 400 psig (2.8 MPag) to 600 psig (4.2 MPag), the effective dewaxing conditions are effective for conversion of 1 wt% to 10 wt% of the at least a portion of the hydroprocessed liquid product effluent, or a combination thereof

4. The method of claim 2, wherein the dewaxed effluent has an aromatics content of 5 wt% to 30 wt%.

5. The method of claim 1, further comprising hydrofining at least a portion of the raffinate product under effective hydrofining conditions to form a hydrofined raffinate, wherein dewaxing at least a first portion of the hydroprocessed liquid product effluent comprises solvent dewaxing at least a portion of the hydrofined raffinate.

6. The method of claim 1, further comprising hydrofinishing at least a portion of the dewaxed effluent under effective hydrofinishing conditions.

7. The method of claim 1, wherein fractionating the at least a portion of the raffinate product further comprises forming a distillate boiling range product.

8. The method of claim 1, further comprising separating the dewaxed effluent to form a fraction having a T5 boiling point of at least 500°F (260°C) and at least one fuel product, the at least one fuel product being a naphtha boiling range product or a distillate fuel boiling range product, wherein extracting at least a portion of the

dewaxed effluent comprises extracting at least a portion of the fraction having a T5 boiling point of at least 500°F (260°C).

9. The method of claim 1, wherein separating the hydroprocessed effluent further comprises forming at least one fuel product, the at least one fuel product being a naphtha boiling range product or a distillate fuel boiling range product.

10. The method of claim 1, wherein the effective hydroprocessing conditions comprise a total pressure of 750 psig (5.2 MPag) to 1500 psig (10.4 MPag), the effective hydroprocessing conditions comprise effective hydrotreating conditions or effective hydrocracking conditions, or a combination thereof.

11. The method of claim 1, wherein the effective hydroprocessing conditions are effective for conversion of 5 wt% to 30 wt% of the feedstock having a T5 boiling point greater than 600°F (316°C) relative to a conversion temperature of 700°F (371°C).

12. The method of claim 1, wherein the hydroprocessed liquid product effluent has a sulfur content of 100 wppm or less.

13. The method of claim 1, wherein the extraction solvent is methyl pyrrolidone (NMP), furfural, phenol, SO₂, sulfolane, dimethylsulfoxide, or combination thereof.

14. A method for forming a lubricant base stock, comprising:

hydroprocessing a feedstock having a T5 boiling point greater than 600°F (316°C) and a sulfur content of at least 500 wppm under effective hydroprocessing

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conditions to form a hydroprocessed effluent, the effective hydroprocessing conditions including a total pressure of less than 1500 psig;

separating the hydroprocessed effluent to form at least a gas phase effluent and a hydroprocessed liquid product effluent having a sulfur content of less than 500 wppm;

exposing at least a portion of the hydroprocessed liquid product effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form a dewaxed effluent, the effective catalytic dewaxing conditions including a total pressure of 300 psig to 700 psig;

extracting at least a portion of the dewaxed effluent in the presence of an extraction solvent to form a raffinate product and an extract product, the raffinate product having a sulfur content of 300 wppm or less; and

fractionating at least a portion of the raffinate product to form at least a lubricant base stock product having a viscosity index of at least 80, and an aromatics content of 2.5 wt% or less.

15. A method for forming a lubricant base stock, comprising:

hydroprocessing a feedstock having a T5 boiling point greater than 600°F (316°C) and a sulfur content of at least 500 wppm under effective hydroprocessing conditions to form a hydroprocessed effluent;

exposing at least a portion of the hydroprocessing effluent to a dewaxing catalyst under effective catalytic dewaxing conditions to form a hydroprocessed, dewaxed effluent, the hydroprocessed, dewaxed effluent comprising a lubricant base oil fraction having an aromatics content of at least 3 wt%, the lubricant base oil fraction including a first lubricant base oil portion and a second lubricant base oil portion;

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exposing the first lubricant base oil portion to an adsorbent to form an aromatics-depleted first lubricant base oil portion, the first lubricant base oil portion comprising 20 wt% to 70 wt% of the lubricant base oil fraction, an aromatics content of the aromatics-depleted first lubricant base oil portion being 500 wppm or less; and

combining the aromatics-depleted first lubricant base oil portion with the second lubricant base oil portion.

16. The method of claim 15, wherein the adsorbent comprises one or more of zeolites, active carbon, mesoporous silica, materials corresponding to the M41S family of materials, and sulfonated polymers.

17. The method of claim 15, wherein the adsorbent comprises one or more of zeolite Beta, USY, zeolite 5A, zeolite 13X, MCM-22, MCM-68, ZSM-5, MCM-41, Amberlyst acid ion exchanged resin and Nafion.

18. The method of claim 15, wherein the adsorbent comprises metal cations, the metal cations comprising cations of Ag, Na, Ca, Cu, or a combination thereof.

19. The method of claim 15, further comprising exposing the adsorbent to a desorption solvent to form an aromatics extract fraction.

20. The method of claim 15, further comprising hydrofinishing at least a portion of the hydroprocessed, dewaxed effluent to form a hydrofinished effluent, the hydrofinished effluent comprising the lubricant base oil fraction.