



(51) International Patent Classification:
C10G 31/00 (2006.01)

(21) International Application Number:
PCT/US201 1/042475

(22) International Filing Date:
30 June 2011 (30.06.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/360,113 30 June 2010 (30.06.2010) US

(71) Applicant (for all designated States except US):
EXXONMOBIL RESEARCH AND ENGINEERING COMPANY [US/US]; 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DOUGHERTY, Richard, Charles** [US/US]; 48 Wagon Bridge Run, Moorestown, NJ 08057-2859 (US). **DAAGE, Michel, A.** [FR/US]; 1847 Viola Lane, Hellertown, PA 18055 (US).

(74) Agents: **BARRETT, Glenn, T.** et al; Exxonmobil Research And Engineering Company, 1545 Route 22 East, P.O. Box 900, Annandale, NJ 08801-0900 (US).

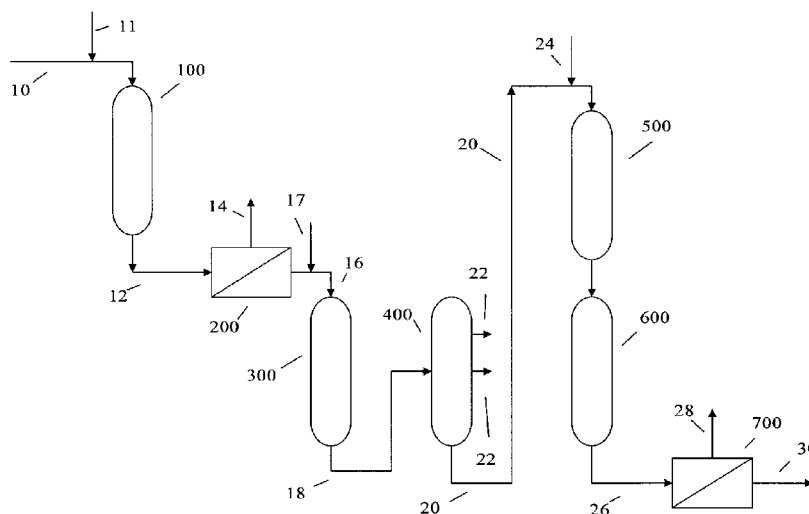
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: PROCESS FOR THE PREPARATION OF GROUP II AND GROUP III LUBE OIL BASE OILS



(57) Abstract: A process for the preparation of Group II and Group III lube oil base stocks wherein liquid-continuous aromatics saturation is used to treat lube hydrocrackate. The treated hydrocrackate is then be sent to dewaxing unit and then optionally to a hydrotreating step.

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**PROCESS FOR THE PREPARATION OF GROUP II
AND GROUP III LUBE OIL BASE OILS**

Field

[0001] This disclosure relates to the preparation of Group II and Group III lube base oils wherein liquid-continuous aromatics saturation is used to treat a lube hydrocrackate. The treated hydrocrackate is then dewaxed and then optionally hydrofinished.

Background

[0002] Crude petroleum is distilled and fractionated into many products such as gasoline, kerosene, jet fuel, asphaltenes, and the like. One portion of the crude petroleum forms the base of lubricating base oils used in, inter alia, the lubricating of internal combustion engines. Lube oil users are demanding ever increasing base oil quality, and refiners are finding that their available equipment is becoming less and less able to produce base oils that meet these higher quality specifications. New processes are required to provide refiners with the tools for preparing high quality modern base oils, particularly using existing equipment at lower cost and with safer operation.

[0003] Finished lubricants used for such things as automobiles, diesel engines, and industrial applications generally are comprised of a lube base oil and additives. In general, a few lube base oils are used to produce a wide variety of finished lubricants by varying the mixtures of individual lube base oils and individual additives. Typically, lube base oils are simply hydrocarbons prepared from petroleum or other sources. Lube base oils are normally

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manufactured by making narrow cuts of vacuum gas oils from a crude vacuum tower. The cut points are set to control the final viscosity and flash point of the lube base oil.

[0004] Group I base oils, those with greater than 300 ppm sulfur and 10 wt.% aromatics are generally produced by first extracting a vacuum gas oil (or waxy distillate) with a polar solvent, such as N-methyl-pyrrolidone, furfural, or phenol. The resulting waxy raffinates produced from solvent extraction process are then dewaxed, either catalytically with the use of a dewaxing catalyst such as ZSM-5, or by solvent dewaxing. The resultant base oil may be hydrofinished to improve color and other lubricant properties.

[0005] Group II base oils, those with less than 300 ppm sulfur and 10 wt.% aromatics, and with a viscosity index range of 80-120, are typically produced by hydrocracking followed by selective catalytic dewaxing and hydrofinishing. Hydrocracking upgrades the viscosity index of the entrained oil in the feedstock by ring cracking and aromatics saturation. The degree of aromatics saturation is limited by the high temperature of the hydrocracking stage. In the second stage of the process, the hydrocracked oil is dewaxed, either by solvent dewaxing or by catalytic dewaxing, with catalytic dewaxing typically being the preferred dewaxing technology. The dewaxed oil is then preferably hydrofinished at mild temperatures to remove polynuclear aromatics which were not converted in the first stage and the dewaxing stage and which have a strongly detrimental impact on lube base oil quality.

[0006] Group III base oils have the same sulfur and aromatics specifications as Group II base stocks but have viscosity indices

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above 120. These materials are manufactured with the same type of catalytic technology employed to produce Group II base oils but with either the hydrocracker being operated at much higher severity, or with the use very waxy feedstocks.

[0007] A typical lube hydroprocessing plant consists of two primary processing stages. In the lead stage, a feedstock, typically a vacuum gas oil, deasphalted oil, processed gas oils, or any combination of these materials, is hydrocracked or solvent extracted. The hydrocracking stage upgrades the viscosity index of the entrained oil in the feedstock by ring cracking and aromatics saturation. The degree of aromatics saturation is limited by the high temperature of the hydrocracking stage. In a second stage, the hydrocracked oil is dewaxed, preferably with the use of a highly shape-selective catalyst capable of wax conversion by isomerization. The dewaxed oil can be subsequently hydrofinished at mild temperatures to remove polynuclear aromatics that were not converted in the upstream hydrocracking and dewaxing stages and which have a strongly detrimental impact on lube base oil quality. Operation of the final hydrofinishing step is optimized to convert polynuclear aromatics; conversion of these species and significant conversion of one ring and two ring aromatics cannot be accomplished in the final hydrofinishing step because of its low operating temperature.

[0008] Group II or III base stocks specifications limit total aromatics content to less than 10 wt.%. However, specific marketing requirements for these materials can be more demanding limiting aromatics contents to 5% or even less. The processing of heavier, more aromatics feedstocks requires a higher degree of aromatics conversion in the hydrocracking and dewaxing zones,

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which is difficult for conventional lube processing technology. There is a need in the art for improved process technology to allow for the use of heavier feeds for the production of Group II and Group III base stocks.

Summary

[0009] In accordance with the present disclosure there is provided a process for the production of lube base oils, which process comprising:

i) hydrocracking a lube oil feedstock having a boiling point above 600°F and containing polycyclic aromatics in the presence of hydrogen and a hydrocracking catalyst to produce a hydrocrackate having a boiling point above 600°F which hydrocrackate contains a lesser amount of polycyclic aromatics than said lube oil feedstock;

ii) hydrotreating at least a portion of said hydrocrackate in the presence of an aromatics saturation catalyst under effective aromatics saturation conditions in a liquid-continuous reactor to form a hydrotreated hydrocrackate having a waxy paraffinic component; and

iii) catalytically dewaxing said hydrotreated hydrocrackate in the presence of hydrogen and a dewaxing catalyst under effective dewaxing conditions including a temperature from 550°F to 800°F and a pressure up to 2200 psig and at an effective contact time of feed to catalyst that will remove at least a portion of the waxy paraffinic components by isomerization to less waxy iso-paraffinic components, thereby producing a lube base oil containing at least

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90 wt.% saturates, less than 0.03 wt.% sulfur and a viscosity index of at least 80.

[0010] In a preferred embodiment, the dewaxed liquid effluent is hydrofinished, by treating it with a hydrofinishing catalyst, in the presence of hydrogen and at effective hydrofinishing conditions that result in the removal of at least a portion of any remaining aromatics, heteroatoms, or both.

Brief Description of the Figure

[0011] The Figure hereof is a simplified flow diagram of a preferred embodiment of the present disclosure showing the primary process units.

Detailed Description

[0012] 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.

[0013] The present disclosure is directed to the preparation of Group II and Group III lube base oils. API Publication 1509: Engine Oil Licensing and Certification System, "Appendix E-API Base Oil Interchangeability Guidelines for Passenger Car Motor Oil and Diesel Engine Oils" describes base stock categories. A Group II base oil will contain greater than or equal to 90 wt.% saturates and less than or equal to 0.03 wt.% sulfur and will have a viscosity index (VI) greater than or equal to 80 and less than 120.

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A Group III base oil will contain greater than or equal to 90 wt.% saturates and less than or equal to 0.03 wt.% sulfur and will have a VI greater than or equal to 120. The VI of an oil is an arbitrary relative measure of the oil's change in viscosity with temperature. The smaller the change in viscosity of an oil at a given temperature the higher the VI value of the oil. A high VI is desirable in high quality motor oils. The term "viscosity index" (VI) refers to the measurement defined by ASTM D2270.

[0014] Lube hydroprocessing refineries are continually challenged to increase throughput and to process more refractory feedstocks. The limitation on refineries to accomplish these objectives is increasingly becoming the refinery's ability to convert aromatics in the feed to meet Group II specification (10 wt.% max) or specific market requirements.

[0015] Both increasing through-put and increasing feed difficulty, work against high aromatics conversion. Increasing throughput and feed aromatics increases the temperature at which hydrocracking must be operated. This limits the amount of aromatics conversion that can occur because of equilibrium constraints. Additionally, increasing throughput and declining feed quality, while increasing the aromatics content of the material entering the dewaxing/hydrotreating zone, also increases the degree of nitrogen slip to this stage. Increases in both aromatics and nitrogen result in lower dewaxing catalyst life, high dewaxing catalyst operating temperature, and less ability of the dewaxing stage to convert aromatics remaining from the hydrocracking zone.

[0016] U.S. Patent No. 5,951,848 teaches the use of a hydrotreating catalyst in the dewaxing reactor upstream of the

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dewaxing catalyst. The purposes of this hydrotreating catalyst, which typically contains a noble metal on an amorphous support (alumina or silica-alumina), are to: a) reduce the aromatics content of the oil reaching the dewaxing catalyst as aromatics have been shown to detrimentally impact dewaxing catalyst life; and b) decouple aromatics saturation from dewaxing so that the exotherm associated with aromatics conversion becomes isolated from the dewaxing catalyst (which has aromatics saturation capability). This allows the dewaxing catalyst to operate more isothermally which increases its life and its selectivity for base oil production.

[0017] Increasing rate and feed refractoriness requires greater dewaxing catalyst volume to maintain cycle length. In a conventional configuration, this would result in displacement of some of the hydrotreating catalyst in the dewaxing reactor which results in less ability to convert aromatics. A solution is represented by the present disclosure with the addition of a hydrocracking reactor, particularly a liquid-continuous reactor, upstream of the dewaxing.

[0018] A typical process scheme for manufacturing Group II base oils from vacuum gas oils includes combining a lube oil feedstock with hydrogen, typically at a rate of 2,000 to 10,000 standard cubic feet per barrel (scf/bbl), and hydrocracking it in the presence of hydrogen and a hydrocracking catalyst, typically in a multi-bed reactor, or in multiple reactors. Hydrocracking is typically operated at a temperature from 600 to 850°F with a liquid flow rate to hydrocracking catalyst volume from 0.2 to 5 liquid hourly space velocity.

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[0019] The nature of hydrocracking catalysts are known to those having ordinary skill in the art and typically contain at least one Group VIII metal, including non-noble metals such as Co and Ni, and noble metals such as Pt and Pd, in combination with at least one Group VIB metal, preferably selected from Mo and W. These metals are supported on a refractory support such as alumina, amorphous silica-alumina, structured aluminosilicates such as zeolites, or a combination of supports. Such catalysts are described in U.S. Pat. No. 3,852,207, which is incorporated herein by reference. The non-noble metals (such as nickel-molybdenum) are usually present in the final catalyst composition as oxides. Preferred non-noble metal catalyst compositions contain in excess of 5 wt.%, preferably 5 wt.% to 40 wt.% molybdenum and/or tungsten, and at least 0.5 wt.%, and generally 1 wt.% to 15 wt.% of nickel and/or cobalt determined as the corresponding oxides, and are converted to sulfide form prior to use. The noble metal (such as platinum) catalysts contain in excess of 0.01 wt.% metal, preferably between 0.1 wt.% to 1 wt.% metal. Combinations of noble metals may also be used, such as mixtures of platinum and palladium. All Groups referred to in this document are groups of the a Periodic Table of the Elements, such as the Sargent-Welch Periodic Table of the Elements copyrighted in 1968 by the Sargent-Welch Scientific Company.

[0020] The product from the hydrocracking reactions is separated into gaseous products, liquid products, and a heavy hydrocrackate. Off-gas from the hydrocracking process is usually purified of contaminant gases such as ammonia and H₂S before being recycled. The hydrocrackate liquid is either stored in tankage before further processing, or is fed directly to a second

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stage of the process. Aromatics reduction during the hydrocracking stage will vary with operating temperature, as set by feed quality and catalyst life within its operating cycle. Aromatics reduction will preferably be at least 50% of the total aromatics in the feed. The pour point of the hydrocrackate will typically be above 80°F, and can often be above 120°F.

[0021] The hydrocracking reactor operation is controlled primarily to meet a finished base oil VI target. Aromatics and nitrogen conversion are also parameters, but have secondary importance in the control of the hydrocracking stage. Because the hydrocracking and dewaxing stages often operate at elevated temperatures that do not favor the conversion of condensed aromatic species, a final low temperature hydrofinishing step is typically employed to reduce the polynuclear aromatics content to improve oxidation stability and color. Because the hydrofinishing stage operates at low temperature, it is not particularly effective at reducing total aromatics. As described above, overall aromatics conversion occurs over each step of the catalytic lubes refining process. Increasing the refractory nature of the feedstock, or increasing throughput, increases the temperature required for both the hydrocracking and dewaxing stages. This makes it more difficult to convert aromatics by conventional processing techniques.

[0022] Feedstocks suitable for use herein may be one or a combination of refinery streams having a normal boiling point of at least 600°F (316°C), although the process is also useful with oils that have initial boiling points as low as 435°F (224°C). By having a normal boiling point of at least 600°F (316°C) is meant that 85%

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by volume of the feedstock has a boiling point at atmospheric pressure of at least 600°F (316°C). While higher boiling lube oil feedstocks can be processed in accordance with the present disclosure, the preferred feedstock will have a boiling range such that at least 85% by volume of the feedstock has a normal boiling point of at most 1250°F (677°C), and more preferably at most 1100°F (593°C). Such feedstocks, particularly vacuum gas oils, will contain from 35 wt.% to 70 wt.% aromatics, at least 40% of them being 2-ring and higher aromatics. Representative feedstocks that can be treated using the present process include gas oils and vacuum gas oils (VGO), hydrocracked gas oils and vacuum gas oils, deasphalted oils, slack waxes, foots oils, coker tower bottoms, reduced crude, vacuum tower bottoms, deasphalted vacuum resids, FCC tower bottoms and cycle oils and raffinates from a solvent extraction process. The nitrogen, sulfur and saturate contents of these feeds will vary depending on a number of factors. The preferred feedstocks for the present disclosure will have an entrained oil viscosity index of greater than 30. In a more preferred embodiment, the entrained oil in the feedstock will have a viscosity index in the range of 40 to 60.

[0023] The process of the present disclosure is better understood with reference to the Figure hereof. This Figure illustrates the primary pieces of equipment for practicing the present disclosure and does not show ancillary equipment, such as valves, pumps, compressors, heat exchanger, heaters and the like. The function of such equipment is well known to those skilled in the art. A lube oil feedstock is conducted to hydrocracking reactor **100** via line **10**. Makeup hydrogen can be added as need via line **11**. Feed molecules are reshaped and some are cracked into

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smaller molecules in hydrocracking reactor 100. Almost all of the sulfur and nitrogen are removed, and aromatic compounds are saturated with hydrogen. Molecular reshaping occurs as isoparaffins and saturated ring compounds are formed. These compounds have high Vis and low pour points. However, waxy compounds, chiefly normal-paraffins are largely unaffected by hydrocracking and must be removed in a subsequent process in order to reduce the pour point.

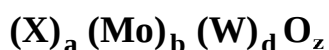
[0024] The resulting hydrocracker effluent is conducted via line 12 to first separation zone 200, which is preferably a hot high-pressure separator wherein a gaseous effluent fraction is separated from a liquid effluent fraction. The gaseous effluent fraction, via line 14, can be treated to remove acidic components and recycled to the hydrocracking reactor 100. The liquid hydrocrackate effluent from first separation zone 200 is passed via line 16 to liquid-continuous aromatics saturation reactor 300. Makeup hydrogen, as needed, can be introduced via line 17. It will be understood that the makeup hydrogen can be added at any suitable point to the feed line or even directly into the reactor 300. It is also within the scope of this disclosure that the liquid effluent from separation zone 200 can be contacted with a fraction of recycle liquid effluent from liquid-continuous aromatics saturation reactor 300, either directly from the reactor, or from a low pressure separator (not shown).

[0025] The liquid effluent from separation zone 200 is also contacted with a hydrogen-rich treat gas in sufficient quantity and in the presence of a suitable aromatics saturation catalyst to saturate at least a fraction of the aromatics of the liquid effluent

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entering reactor **300**. Catalysts suitable for use in liquid-continuous aromatics saturation reactor **300** can comprise a support component and one or catalytic metal components of metal from Groups VIB (Mo, W, Cr) and/or non-noble (Co, Ni) and noble metals, such as Pt and Pd from Group VIII. The metal or metals may be present from as little as 0.1 wt % for noble metals, to as high as 40 wt % of the catalyst composition for supported non-noble metals. Preferred support materials are low in acid and include, for example, amorphous or crystalline metal oxides such as alumina, silica, silica alumina, titania, zirconia, silica-alumina and ultra large pore crystalline materials known as mesoporous crystalline materials, of which MCM-41 is a preferred support component. The preparation and use of MCM-41 is disclosed, for example, in U.S. Pat. Nos. 5,098,684, 5,227,353 and 5,573,657, both of which are incorporated herein by reference.

[0026] Bulk multimetallic catalysts can also be used for aromatics saturation in the practice of the present disclosure. Such catalysts are described in U.S. Patent Nos. 6,156,695; 6,162,350; and 6,299,760, all of which are incorporated herein by reference. The catalysts described in these patents are bulk multimetallic catalysts comprised of at least one Group VIII non-noble metal and at least two Group VIB metals, wherein the ratio of Group VIB metal to Group VIII non-noble metal is from 10:1 to 1:10. These catalysts are prepared from a precursor having the formula:



where X is a Group VIII non noble metal, wherein the molar ratio of and a, b, and c, are such that $0.1 < (b+c)/a < 10$, and $z = [2a + 6(b+c)]/2$. The precursor has x-ray diffraction peaks at $d = 2.53$ and

1.70 Angstroms. The precursor is sulfided to produce the corresponding activated catalyst.

[0027] It is also within the scope of this disclosure that the gas-liquid flow to liquid-continuous aromatics saturation reactor **300** be blended under static mixing conditions. By static mixing conditions we mean one or more, preferably more, of geometric mixing elements fixed within a pipe that use the energy of the moving stream to create mixing between two or more fluids. The advantage of the static mixers of the present disclosure over dynamic mixers, other than the fact that static mixers have no moving parts, is that static mixers split the stream hundreds, or even thousands of times, thus resulting in a continuous phase containing very fine droplets of discontinuous phase. This results in a much larger surface area when compared with dynamic mixers. The gas-liquid mixture can also be flashed in a suitable vessel before entering reactor **300** to remove at least a portion of any excess gas. Alternatively, excess gas can be vented (not shown) directly from reactor **300**.

[0028] To ensure that sufficient hydrogen is present in the liquid phase for reaction, and to mitigate coking, it may be necessary to recycle liquid product from the liquid-continuous aromatics saturation reactor **300**. The recycled liquid serves as a carrier for additional solubilized hydrogen. Alternatively, or in combination with this liquid recycle, hydrogen may be added to the reactor by withdrawing liquid at one or more points, preferably at one or more axial points, along the reactor, resaturating the liquid with hydrogen, and reinjecting it back into the reactor. This

approach may be used to reduce the amount of liquid recycle required.

[0029] Because the liquid effluent from the reactor **300** contains only dissolved gas, it is not necessary to have a high-pressure separation step downstream of the reactor. Only a low-pressure flash step is required to vent dissolved and excess gas before product fractionation. Elimination of high-pressure product recovery vessels significantly reduces the cost of the debottlenecking.

[0030] As previously mentioned, reactor **300** is operated such that the liquid phase represents the continuous phase in the reactor. Traditionally, hydroprocessing, including aromatics saturation, is conducted in trickle-bed reactors where an excess of gas results in a continuous gas phase in the reactor. In a liquid-continuous reactor, the feedstock is exposed to one or more beds of catalyst. The liquid hydrocrackate preferably enters from the top or upper portions of the reactor and flows downward through the reactor. This downward liquid flow can assist in allowing the catalyst to remain in place in the catalyst bed.

[0031] A hydroprocessing process can typically involve exposing a feed to a suitable catalyst in the presence of hydrogen at effective hydroprocessing conditions. Without being bound by any particular theory, in a conventional trickle-bed reactor, the reactor can be operated so that three "phases" are present in the reactor. The hydroprocessing catalyst corresponds to the solid phase. Another substantial portion of the reactor volume is occupied by a gas phase. This gas phase (second-phase) includes the hydrogen for hydroprocessing, optionally some diluent gases, and other gases

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such as contaminant gases that are formed during hydroprocessing. The amount of hydrogen gas in the gas phase is typically present in substantial excess relative to the amount required for the hydroprocessing reaction. In a conventional trickle-bed reactor, the solid hydroprocessing catalyst and the gas phase can occupy at least 80% of the reactor volume, or at least 85%, or at least 90%. The third "phase" can correspond to the liquid feedstock. In a conventional trickle-bed reactor, the feedstock may only occupy a small portion of the volume, such as less than 20%, or less than 10%, or less than 5%. As a result, the liquid feedstock may not form a continuous phase. Instead, the liquid "phase" may include, for example, thin films of feedstock that coat the hydroprocessing catalyst particles.

[0032] Without being bound by any particular theory, a liquid-continuous reactor provides a different type of processing environment as compared to a trickle-bed reactor. In a liquid-continuous reactor, the reaction zone is primarily composed of two phases. One phase is a solid phase corresponding to the hydroprocessing catalyst, in this case an aromatics saturation (ASAT) catalyst. The second phase is a liquid phase corresponding to the hydrocrackate feedstock. The liquid feedstock phase will be present as a continuous phase in the liquid-continuous reactor of the present disclosure. In an embodiment, the hydrogen that will be consumed during the aromatic saturation reaction is dissolved in the liquid phase. Depending on the quantity of hydrogen used, a portion of the hydrogen can also be in the form of bubbles of hydrogen in the liquid phase. This hydrogen corresponds to hydrogen that is in addition to the hydrogen dissolved in the liquid phase. In another embodiment,

hydrogen dissolved in the liquid phase can be depleted as the reactions progress in the liquid-continuous reactor. In such an embodiment, hydrogen initially present in the form of gaseous bubbles can dissolve into the liquid phase to resaturate the liquid phase and provide additional hydrogen for the reactions taking place in the reactor. In various embodiments, the volume occupied by a gas phase in the liquid-continuous reactor can be less than 10% of the reactor volume, or even less than 5%.

[0033] The liquid feed to reactor 300 is preferably mixed with a hydrogen-containing treat gas. The hydrogen-containing treat gas will preferably contain at least 50 vol% of hydrogen, more preferably at least 80 vol%, even more preferably at least 90 vol%, and most preferably at least 95 vol%. Excess gas can be vented from the mixture before it enters the reactor, or excess gas can be vented directly from the reactor. The liquid level in the reactor is preferably controlled so that the catalyst in the reactor is completely wetted.

[0034] In some embodiments, the hydroprocessing reactions in a bed, stage, and/or reactor can require more hydrogen than can be dissolved in a liquid. In such embodiments, one or more techniques can be used to provide additional hydrogen for the hydroprocessing reaction. One option is to recycle a portion of the product from the reactor. A recycled portion of product has already passed through a hydroprocessing stage, and therefore will likely have a reduced hydrogen consumption as it passes again through the hydroprocessing stage. Additionally, the solubility of the recycled feed can be higher than a comparable unprocessed feed. As a result, including a portion of recycled product with

fresh feed can increase the amount of hydrogen available for reaction with the fresh feed.

[0035] Another option can be to introduce additional streams of hydrogen into the reactor directly. One or more additional hydrogen streams can be introduced at any convenient location in the reactor. The additional hydrogen streams can include a stream of make-up hydrogen, a stream of recycled hydrogen, or any other convenient hydrogen-containing stream. In some embodiments, both product recycle and injection of additional hydrogen streams along the axial dimension of the reactor can be used to provide sufficient hydrogen for a reaction.

[0036] In embodiments involving recycle of the product from liquid-continuous aromatics saturation zone **300** can be used as part of the input to the liquid-continuous aromatics saturation zone, or, reactor **300**. The ratio of the amount by volume of product recycle to the amount of fresh feed into the zone **300** can be at least 0.5 to 1, or at least 1 to 1, or at least 1.5 to 1. The ratio of the amount by volume of product recycle to the amount of fresh feed can be 5 to 1 or less, or 3 to 1 or less, or 2 to 1 or less.

[0037] Aromatics saturation is performed by exposing a feedstock to an aromatics saturation catalyst under effective aromatics saturation conditions. Effective aromatics saturation conditions can include a temperature of at least 400°F (204°C), or at least 450°F (232°C), or at least 500°F (260°C). Alternatively, the temperature can be 750°F (399°C) or less, or 700°F (371°C) or less, or 650°F (343°C) or less. The pressure can be at least 500 psig (3.3 MPa), or at least 800 psig (5.3 MPa), or at least 1000 psig (6.6 MPa). Alternatively, the pressure can be 2500 psig (16.6

MPa) or less, or 2000 psig (13.3 MPa) or less, or 1500 psig (10 MPa) or less. The liquid hourly space velocity (LHSV) over the dewaxing catalyst can be at least 0.25 hr^{-1} , or at least 0.5 hr^{-1} , or at least 0.75 hr^{-1} . Alternatively, the LHSV can be 15 hr^{-1} or less, or 10 hr^{-1} or less, or 5 hr^{-1} or less. In still another embodiment, the temperature, pressure, and LHSV for a liquid-continuous reactor can be conditions suitable for use in a trickle-bed reactor.

[0038] In embodiments where excess gas is vented from the liquid effluent, the available hydrogen in the reactor will correspond to the amount of hydrogen dissolved in the liquid. Thus, a higher treat gas rate may not lead to an increase in the amount of available hydrogen. In such a situation, the effective treat gas rate within a reactor may be dependent on the solubility limit of the feedstock. The hydrogen solubility limit for a typical hydrocarbon feedstock is 30 scf/bbl to 200 scf/bbl.

[0039] One advantage of a liquid-continuous reactor is that a large excess of hydrogen is not fed to the reactor. The use of a large excess of hydrogen typically requires complex and expensive separation equipment to allow for recovery, and often recycling, of the excess hydrogen. Typically, the recycle compressor used for hydrogen recycle in a trickle-bed reactor corresponds to 10 to 15 wt.% of the total cost of the processing unit. Instead, it is desirable for a liquid-continuous reactor will desirably supply only an amount of hydrogen comparable to the amount needed for a hydroprocessing reaction and to mitigate catalyst coking.

[0040] Returning now to the Figure hereof, the effluent stream from **300** is conducted via line **18** to fractionator **400** wherein a lube oil liquid effluent fraction is separated and passed via line **20**

to catalytic dewaxing stage **500**. Make-up hydrogen-containing treat gas can be introduced via line **24** when needed. Any predetermined additional fractions can be separated and are collected from fractionator **400** via lines **22**. It will be understood that catalytic dewaxing stage **500** can also be operated in liquid-continuous mode. It is within the scope of this disclosure that the liquid effluent from the liquid-continuous aromatics saturation zone can be conducted directly to catalytic dewaxing and the effluent from catalytic dewaxing fractionated.

[0041] Catalytic dewaxing can be performed by exposing the feedstock to a dewaxing catalyst under effective (catalytic) dewaxing conditions. Effective dewaxing conditions can include a temperature of at least 500°F (260°C), or at least 550°F (288°C), or at least 600°F (316°C), or at least 650°F (343°C). Alternatively, the temperature can be 750°F (399°C) or less, or 700°F (371°C) or less, or 650°F (343°C) or less. The pressure can be at least 200 psig (1.4 MPa), or at least 400 psig (2.8 MPa), or at least 750 psig (5.2 MPa), or at least 1000 psig (6.9 MPa). Alternatively, the pressure can be 1500 psig (10.3 MPa) or less, or 1200 psig (8.2 MPa) or less, or 1000 psig (6.9 MPa) or less, or 800 psig (5.5 MPa) or less. The liquid hourly space velocity (LHSV) over the dewaxing catalyst can be at least 0.1 hr⁻¹, or at least 0.2 hr⁻¹, or at least 0.5 hr⁻¹, or at least 1.0 hr⁻¹, or at least 1.5 hr⁻¹. Alternatively, the LHSV can be 10.0 hr⁻¹ or less, or 5.0 hr⁻¹ or less, or 3.0 hr⁻¹ or less, or 2.0 hr⁻¹ or less. In still another embodiment, the temperature, pressure, and LHSV for a liquid-continuous reactor can be the same conditions typically used for a trickle-bed reactor.

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[0042] Catalytic dewaxing involves the removal and/or isomerization of long chain, paraffinic molecules from feeds. Catalytic dewaxing can be accomplished by selective cracking or by hydroisomerizing these linear molecules. Hydrodewaxing catalysts can be selected from molecular sieves such as crystalline aluminosilicates (zeolites) or silico-aluminophosphates (SAPOs). In an embodiment, the molecular sieve can be a 1-D or 3-D molecular sieve. In another embodiment, the molecular sieve can be a 10-member ring 1-D molecular sieve. Examples of molecular sieves which have shown dewaxing activity in the literature can include ZSM-48, ZSM-22, ZSM-23, ZSM-35, Beta, USY, ZSM-5, and combinations thereof. In an embodiment, the molecular sieve can be ZSM-22, ZSM-23, ZSM-35, ZSM-48, or a combination thereof. In still another embodiment, the molecular sieve can be ZSM-48, ZSM-23, ZSM-5, or a combination thereof. In yet another embodiment, the molecular sieve can be ZSM-48, ZSM-23, or a combination thereof. Optionally, the dewaxing catalyst can include a binder for the molecular sieve, such as alumina, titania, silica, silica-alumina, zirconia, or a combination thereof.

[0043] One feature of molecular sieves that can impact the activity of the molecular sieve is the ratio of silica to alumina in the molecular sieve. In an embodiment, the molecular sieve can have a silica to alumina ratio of 200 to 1 or less, or 120 to 1 or less, or 100 to 1 or less, or 90 to 1 or less, or 75 to 1 or less. In an embodiment, the molecular sieve can have a silica to alumina ratio of at least 30 to 1, or at least 50 to 1, or at least 65 to 1.

[0044] The dewaxing catalyst can also include a metal hydrogenation component, such as a Group VIII metal. Suitable Group VIII metals can include Pt, Pd, Ni, or a combination thereof. The dewaxing catalyst can include at least 0.1 wt% of a Group VIII metal, or at least 0.3 wt%, or at least 0.5 wt%, or at least 1.0 wt%, or at least 2.5 wt%, or at least 5.0 wt%. Alternatively, the dewaxing catalyst can include 10.0 wt% or less of a Group VIII metal, or 5.0 wt% or less, or 2.5 wt% or less, or 1.5 wt% or less, or 1.0 wt% or less.

[0045] In some embodiments, the dewaxing catalyst can also include at least one Group VIB metal, such as W or Mo. Such Group VIB metals are typically used in conjunction with at least one Group VIII metal, such as Ni or Co. An example of such an embodiment is a dewaxing catalyst that includes Ni and W, Mo, or a combination of W and Mo. In such an embodiment, the dewaxing catalyst can include at least 0.5 wt% of a Group VIB metal, or at least 1.0 wt%, or at least 2.5 wt%, or at least 5.0 wt%. Alternatively, the dewaxing catalyst can include 20.0 wt% or less of a Group VIB metal, or 15.0 wt% or less, or 10.0 wt% or less, or 5.0 wt% or less, or 1.0 wt% or less. In an embodiment, the dewaxing catalyst can include Pt, Pd, or a combination thereof. In another embodiment, the dewaxing catalyst can include Co and Mo, Ni and W, Ni and Mo, or Ni, W, and Mo.

[0046] The catalytic dewaxer can be operated at pressures significantly lower than the hydrocracker. That is, at least 300 psi, or at least 500 psi, and even at least 1000 psi lower than the hydrocracking stage. Both stages being high pressure is far more common and consistent with high quality lube production.

[0047] Returning again to the Figure hereof, the effluent from catalytic dewaxing stage **500** is sent to hydrofinishing stage **600**. The hydrofinishing step following dewaxing offers further opportunity to improve product quality without significantly affecting its pour point. Hydrofinishing is a mild, relatively cold hydrotreating process, that employs a catalyst, hydrogen and mild reaction conditions to remove trace amounts of heteroatom compounds, aromatics and olefins, to improve primarily oxidation stability and color. Hydrofinishing reaction conditions include temperatures from 300°F to 675°F (149°C to 357°C), preferably from 300°F to 480°F. (149°C to 249°C), a total pressure of from 400 to 3000 psig (2859 to 20786 kPa), a liquid hourly space velocity ranging from 0.1 to 5 LHSV (hr^{-1}), preferably 0.5 to 3 hr^{-1} . The hydrotreating catalyst will comprise a support component and one or more catalytic metal components. The one or more metals are selected from Group VIB (Mo, W, Cr) and Group VIII (Ni, Co and the noble metals Pt and Pd). The metal or metals may be present from as little as 0.1 wt % for noble metals, to as high as 30 wt % of the catalyst composition for non-noble metals. Preferred support materials are low in acid and include, for example, amorphous or crystalline metal oxides such as alumina, silica, silica alumina and ultra large pore crystalline materials known as mesoporous crystalline materials, of which MCM-41 is a preferred support component. Unsupported base metal (non-noble metal) catalysts are also applicable as hydrofinishing catalysts.

[0048] The effluent stream from hydrofinishing zone **600** is passed via line **26** to second separation zone **700** wherein a gaseous effluent stream is separated from the resulting liquid phase lube oil base stock. The gaseous effluent stream, a portion of which will be

unreacted hydrogen-containing treat gas can be recycled via line **28** to hydrocracking stage **100**. The resulting lube oil base stock, which will meet Group II or Group III base oil requirements, is collected via line **30**.

[0049] All patents and patent applications, test procedures (such as ASTM methods, UL methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this disclosure and for all jurisdictions in which such incorporation is permitted.

[0050] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. While the 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.

[0051] 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.

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CLAIMS:

1. A process for the production of high quality lube base oils, which process comprising:

i) hydrocracking a lube oil feedstock having a boiling point above 600°F and containing polycyclic aromatics in the presence of hydrogen and a hydrocracking catalyst to produce a hydrocrackate having a boiling point above 600°F which hydrocrackate contains a lesser amount of polycyclic aromatics than said lube oil feedstock;

ii) hydrotreating at least a portion of said hydrocrackate in the presence of an aromatics saturation catalyst under effective aromatics saturation conditions in a liquid-continuous reactor to form a hydrotreated hydrocrackate having a waxy paraffinic component; and

iii) catalytically dewaxing said hydrotreated hydrocrackate in the presence of hydrogen and a dewaxing catalyst under effective dewaxing conditions including a temperature from 500°F to 750°F and a pressure up to 2200 psig and at an effective contact time of feed to catalyst that will remove at least a portion of the waxy paraffinic components by isomerization to less waxy iso-paraffinic components, thereby producing a lube base oil containing of at least 90 wt.% saturates, less than 0.03 wt.% sulfur and a viscosity index of at least 80.

2. The process of claim 1 wherein the lube oil feedstock is selected from the group consisting of vacuum gas oils, hydrocracked gas oils, hydrocracked vacuum gas oils, deasphalted oils, slack waxes, foots oils, coker tower bottoms, reduced crude, vacuum tower

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bottoms, deasphalted vacuum resids, fluid catalytic cracking tower bottoms, and cycle oils.

3. The process of claim 2 wherein the lube oil feedstock is a vacuum gas oil.

4. The process of claim 1 wherein a portion of the hydrotreated hydrocrackate is recycled to the liquid-continuous reactor and again hydrotreated with fresh hydrocrackate.

5. The process of claim 4 wherein the volume ratio of recycled hydrotreated hydrocrackate to fresh hydrocrackate to the liquid-continuous reactor is from 0.5 to 1 to 5 to 1.

6. The process of claim 4 wherein the volume ratio of recycled hydrotreated hydrocrackate to fresh hydrocrackate to the liquid-continuous reactor is from 1 to 1 to 3 to 1.

7. The process of claim 1 wherein a portion of the hydrotreated hydrocrackate from the liquid-continuous reactor is withdrawn and saturated with hydrogen then recycled back to the liquid-continuous reactor.

8. The process of claim 1 wherein the aromatics saturation catalyst is comprised of one or more catalytic metals selected from Groups VIB and Group VIII of the Periodic Table of the Elements on an amorphous or crystalline refractory support.

9. The process of claim 8 wherein the support is a mesoporous material.

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10. The process of claim 9 wherein the mesoporous material is MCM-41.
11. The process of claim 9 wherein the catalytic metal is selected from the group consisting of Pt and Pd.
12. The process of claim 1 wherein the hydrocracking of step i) results in at least a 50% reduction of aromatics compared to the amount of aromatics in the lube oil feedstock.
13. The process of claim 1 wherein the process conditions for aromatics saturation during hydrotreating includes temperatures from 400°F to 750°F and pressures from 500 psig to 2500 psig.
14. The process of claim 1 wherein the catalytic dewaxing temperature is from 500°F to 750°F.
15. The process of claim 1 wherein the catalytic dewaxing catalyst is selected from the group consisting of crystalline aluminosilicates and silicoaluminophosphates.
16. The process of claim 15 wherein the catalytic dewaxing catalyst is a crystalline aluminosilicate selected from the group consisting of ZSM-22, ZSM-23, ZSM-35 and ZSM-48, and combinations thereof.
17. The process of claim 16 wherein the catalytic dewaxing catalyst contains a binder material selected from the group consisting of alumina, titania, silica, silica-alumina, zirconia, and combinations thereof.

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18. The process of claim 16 wherein the catalytic dewaxing catalyst contains at least one metal selected from the group consisting of Pt, Pd, and Ni.
19. The process of claim 18 wherein the catalytic dewaxing catalyst also contains a metal selected from W and Mo.
20. The process of claim 1 wherein the dewaxed lube oil is subjected to hydro finishing in the presence of hydrogen and a hydrofinishing catalyst at a temperature from 300°F to 675°F and total pressures from 400 to 3000 psig.
21. The process of claim 20 wherein the hydrofinishing catalyst is comprised of one or more metals selected from Group VIII and Group VIB of the Periodic Table of the Elements.
22. The process of claim 21 wherein the hydrofinishing catalyst contains at least one metal from Group VIII and at least one metal from Group VIB.
23. The process of claim 21 wherein the hydrofinishing catalyst is comprised of a noble metal selected from Pt and Pd on a mesoporous crystalline support.
24. The process of claim 23 wherein the mesoporous crystalline support is MCM-41.
25. A process for the production of high quality lube base oils, which process comprising:
 - i) hydrocracking a lube oil feedstock having a boiling point above 600°F and containing polycyclic aromatics in the presence

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of hydrogen and a hydrocracking catalyst to produce a hydrocrackate having a boiling point above 600°F which contains a lesser amount of polycyclic aromatics than said lube oil feedstock;

ii) hydrotreating at least a portion of said hydrocrackate in the presence of an aromatics saturation catalyst under effective aromatics saturation conditions in a liquid-continuous reactor to form a hydrotreated hydrocrackate having a waxy paraffinic component;

iii) catalytically dewaxing said hydrotreated hydrocrackate in the presence of hydrogen and a dewaxing catalyst under effective dewaxing conditions including a temperature from 500°F to 750°F and a pressure up to 2200 psig and at an effective contact time of feed to catalyst that will remove at least a portion of the waxy paraffinic components by isomerization to less waxy iso-paraffinic components; and

iv) subjecting the dewaxed hydrotreated hydrocrackate to hydrofinishing in the presence of hydrogen and a hydrofinishing catalyst and at hydrofinishing conditions thereby resulting in a lube base oil comprised of at least 90 wt.% saturates, less than 0.03 wt.% sulfur and a viscosity index of at least 80.

26. The process of claim 25 wherein the lube oil feedstock is selected from the group consisting of vacuum gas oils, hydrocracked gas oils, hydrocracked vacuum gas oils, deasphalted oils, slack waxes, foots oils, coker tower bottoms, reduced crude, vacuum tower bottoms, deasphalted vacuum resids, fluid catalytic cracking tower bottoms, and cycle oils.

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27. The process of claim 26 wherein the lube oil feedstock is a vacuum gas oil.

28. The process of claim 26 wherein a portion of the hydrotreated hydrocrackate is recycled to the liquid-continuous reactor and again hydrotreated with fresh hydrocrackate.

29. The process of claim 28 wherein the volume ratio of recycled hydrotreated hydrocrackate to fresh hydrocrackate to the liquid-continuous reactor is from 0.5 to 1 to 5 to 1.

30. The process of claim 28 wherein the volume ratio of recycled hydrotreated hydrocrackate to fresh hydrocrackate to the liquid-continuous reactor is from 1 to 1 to 3 to 1.

31. The process of claim 25 wherein a portion of the hydrotreated hydrocrackate from the liquid-continuous reactor is withdrawn and saturated with hydrogen then recycled back to the liquid-continuous reactor.

32. The process of claim 25 wherein the aromatics saturation catalyst is comprised of one or more catalytic metals selected from Groups VIB and Group VIII of the Periodic Table of the Elements on an amorphous or crystalline refractory support.

33. The process of claim 32 wherein the support is a mesoporous material.

34. The process of claim 33 wherein the mesoporous material is MCM-41.

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35. The process of claim 33 wherein the catalytic metal is selected from the group consisting of Pt and Pd.

36. The process of claim 25 wherein the hydrocracking of step i) results in at least a 50% reduction of aromatics compared to the amount of aromatics in the lube oil feedstock.

37. The process of claim 25 wherein the process conditions for aromatics saturation during hydrotreating includes temperatures from 400°F to 750°F and pressures from 500 psig to 2500 psig.

38. The process of claim 25 wherein the catalytic dewaxing temperature is from 500°F to 750°F.

39. The process of claim 25 wherein the catalytic dewaxing catalyst are selected from the group consisting of crystalline aluminosilicates and silicoaluminophosphates.

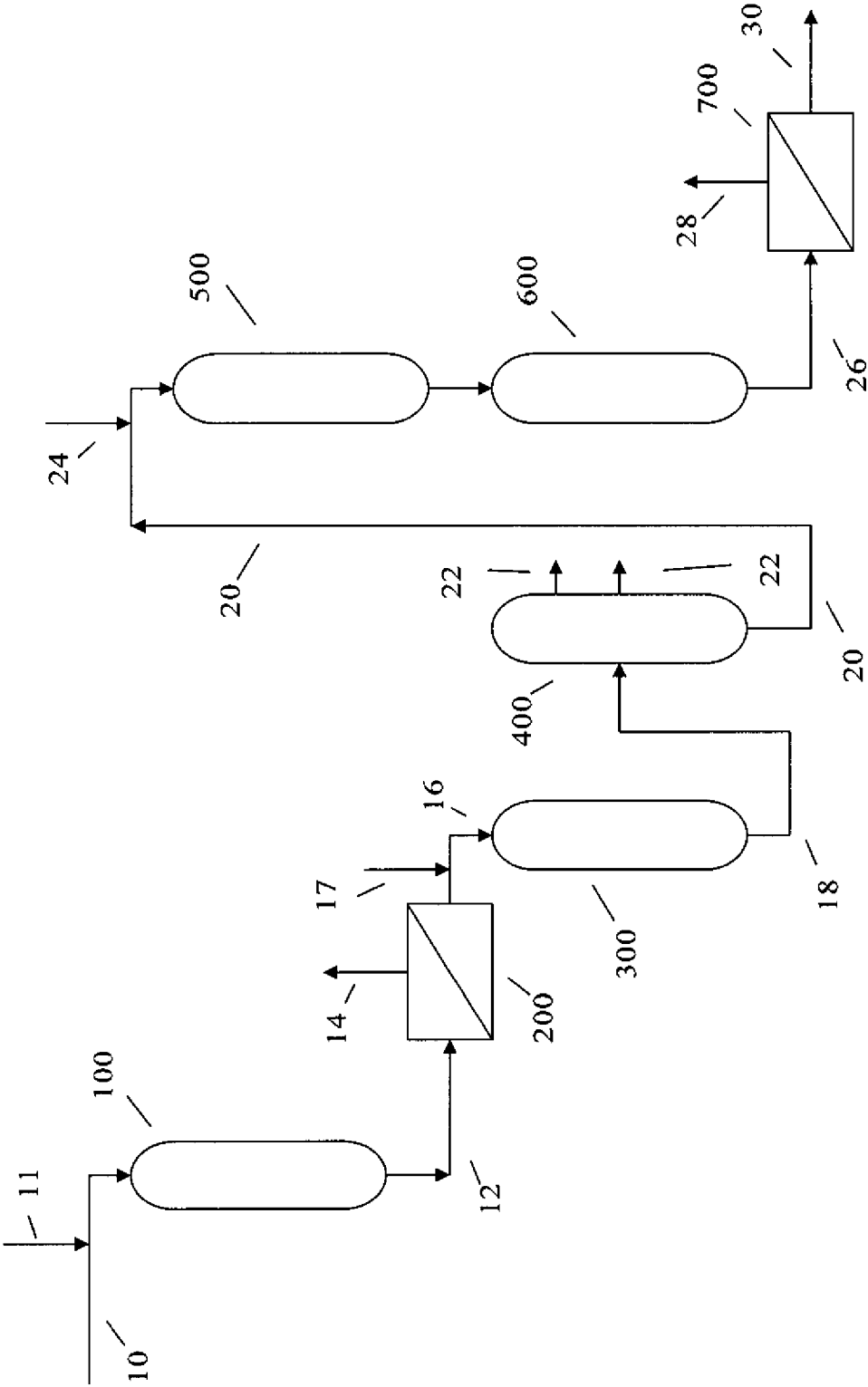
40. The process of claim 39 wherein the catalytic dewaxing catalyst is a crystalline aluminosilicate selected from the group consisting of ZSM-22, ZSM-23, ZSM-35 and ZSM-48, and combinations thereof.

41. The process of claim 40 wherein the catalytic dewaxing catalyst contains a binder material selected from the group consisting of alumina, titania, silica, silica-alumina, zirconia, and combinations thereof.

42. The process of claim 40 wherein the catalytic dewaxing catalyst contains at least one metal selected from the group consisting of Pt, Pd, and Ni.

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43. The process of claim 42 wherein the catalytic dewaxing catalyst also contains a metal selected from W and Mo.
44. The process of claim 25 wherein the hydrofinishing catalyst is comprised of one or more metals selected from Group VIII and Group VI of the Periodic Table of the Elements.
45. The process of claim 44 wherein the hydrofinishing catalyst contains at least one metal from Group VIII and at least one metal from Group VIB.
46. The process of claim 44 wherein the hydrofinishing catalyst is comprised of a noble metal selected from Pt and Pd on a mesoporous crystalline support.
47. The process of claim 46 wherein the mesoporous crystalline support is MCM-41.



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 11/42475

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C10G 31/00 (201 1.01)

USPC - 208/28; 208/18; 208/1 34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8): C10G 31/00 (201 1.01); USPC: 208/28; 208/18; 208/134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC: 208/28; 208/18; 208/134

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Google Scholar, Google Patents, PubWEST (PGPB,USPT,EPAB,JPAB) Lubricate, oil, aromatic, hydrocracking, dewaxing, hydrotreating, petroleum, distill, fractionate, sulfur, catalyst, polycyclic, aromatic, deasphalted, crude, vacuum, gas, hydrogen, mesoporous, amorphous, crystalline, support, Pt, Pd, Ni, ZSM, MCM, alumina, titania, silica, isomerize

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2009/0159492 A1 (Duhoux, et al.) 25 Jun 2009 (25.06.2009) paragraphs [0024]-[0035], [0040], [0049]-[0054], [0062]-[0067], [0070]-[0078], [0097]	1-47
Y	US 3,441,500 A (Wunderlich, et al.) 29 Apr 1969 (29.04.1969) column 4, line 66-71	1-47

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

14 Oct 2011 (14.10.2011)

Date of mailing of the international search report

28 OCT 2011

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774