PROCESS FOR PRODUCING LUBRICANT BASE OILS

FIELD OF THE INVENTION

[0002] The present invention is an improved process for producing lubricant base oils. More particularly, the instant invention is an improved process for producing naphthenic base oils from low quality feedstocks.

BACKGROUND OF THE INVENTION

[0003] End-users of process oils are requesting increased solvency of these products as indicated by lower aniline point requirements. Simultaneously, the availability and supply of conventional naphthenic crude oil sources is declining. Thus, there exists a need in the art for a process that produces naphthenic base oils, particularly those base oils having a lower aniline point, from a lesser amount of naphthenic distillate.

[0004] United States Patent Numbers 4,744,884, and 4,699,707, both to Moorehead, et al. disclose a process to produce lubricating oil fractions boiling above 650°F(343.3°C) having a pour point at or below 10°F(-12.2°C) and a viscosity index of at least 95. The process comprises hydrotreating a full-range shale oil and then hydrodewaxing the effluent from the hydrotreating step. The product from the hydrodewaxing step is passed to a hydrogenation reactor wherein it is contacted with a catalyst containing a hydrogenation metal

component. After hydrogenating the product from the hydrogenation stage is fractionated into one or more lubricating oil fractions.

[0005] United States Patent Number 5,976,354, Powers, et al. discloses a process whereby the practitioner can produce a diesel fraction, light oil fraction, and a finished oil. The process comprises the steps of mild hydrotreating, followed by catalytic dewaxing, and an optional aromatics saturation step after the catalytic dewaxing. The product from the catalytic dewaxing, or from the optional aromatics saturation step, is sent to a fractionation tower to separate the products. All of the above-cited references are hereby incorporated by reference.

[0006] There still exists a need in the art for a process that produces naphthenic base oils, particularly those base oils having a low aniline point, from a low quality feedstock.

SUMMARY OF THE INVENTION

[0007] The instant invention is a process for producing at least one naphthenic base oil having a low aniline point from a hydrocarbon feedstock containing heteroatom species and aromatics and boiling in the gas oil range, said process comprising:

a) hydrofining said feedstock under hydrofining conditions effective for removing at least a portion of the heteroatom species and saturating at least a portion of said aromatics to produce a first stage effluent having a reduced amount of heteroatom species;

b) stripping said first stage effluent to remove at least a portion of lower boiling hydrocarbons and hydrogen sulfide in a stripping column wherein at least one intermediate stream is removed from said stripping column;

c) dewaxing said intermediate stream in a catalytic dewaxing unit to produce at least one second stage effluent containing heteroatom species;

d) hydrotreating said second stage effluent under hydrotreating conditions effective for removing at least a portion of the heteroatom species to produce at least one third stage effluent having a reduced amount of heteroatom species; and

e) fractionating said third stage effluent to produce at least one naphthenic base oil.

[0008] In one embodiment at least two base oils having low aniline points are produced from a hydrocarbon feedstock comprising a mixture of several refinery streams selected from coker gas oil, lube extracts, deasphalted oil, fuels distillates, and cracker resids, said hydrocarbon feedstock containing heteroatom species and aromatics and boiling in the range of 150°C to 550°C

[0009] In another embodiment at least three base oils having low aniline points are produced from a hydrocarbon feedstock comprising a mixture of several refinery streams selected from coker gas oil, lube extracts, deasphalted oil, fuels distillates, and cracker resids, said hydrocarbon feedstock containing heteroatom species and aromatics and boiling in the range of 150°C to 550°C

DETAILED DESCRIPTION OF THE INSTANT INVENTION

[0010] The present invention is a process for producing at least one naphthenic base oil from a hydrocarbon feedstock boiling in the gas oil range. By naphthenic it is meant a base oil having a viscosity index of less than 85 and wherein at least 30% of the carbon bonds of the base oil are of the naphthenic type as defined by ASTM D 2140. The feedstock is first hydrofined under effective conditions to remove or convert at least a portion of the heteroatom species that are present in the feedstock, and the hydrofining step also saturates at least a portion of the aromatics present in the feedstock. Thus, the hydrofining step produces a first stage effluent that has a reduced amount of heteroatom contaminants and saturated aromatics. After hydrofining, the first stage effluent is passed to a stripping stage to remove lighter hydrocarbon components and hydrogen sulfide through the use of a conventional stripper. The preferred stripper used has at least one reflux tray and at least one feed tray. During the

stripping stage, at least one intermediate stream is removed from the stripper at a point between the reflux tray and the feed tray. The intermediate stream is catalytic dewaxed in a dewaxing stage, sometimes referred to herein as a dewaxing zone, to produce a second stage effluent, and the second stage effluent is then hydrotreated to produce at least one third stage effluent having a reduced amount of heteroatom species. The third stage effluent is subsequently passed to a fractionation zone wherein at least one naphthenic base oil is produced. It should be noted that naphthenic base oils are characterized by having an aniline point at a given viscosity lower than a more paraffinic base oil of the same viscosity.

[0011] The feedstock used in the instant process boils in the gas oil range, 150°C to 550°C, and contains aromatics and undesirable heteroatom species. The feedstock can be a mixture of several less desirable refinery streams such as, for example, coker gas oil, lube extracts, deasphalted oil, fuels distillates, and cracker resids, and it is preferred that the instant process be used to treat such less desirable refinery streams.

[0012] The feedstock is first passed to a hydrofining stage, sometimes referred to herein as a first stage or zone. Hydrofining typically removes sulfur and nitrogen polar compounds and results in some saturation of aromatic

compounds such as thiophene. It should be noted that some degree of cracking also occurs in the hydrofining stage. Thus, the first stage produces a first stage effluent having at least a portion of the aromatics present in the feedstock saturated, and a decreased concentration of sulfur heteroatom compounds and nitrogen heteroatom compounds. The hydrofining process can be carried out by contacting the feedstock with a catalytically effective amount of a hydrofining catalyst in the presence of hydrogen under suitable hydrofining conditions. The hydrofining process can be carried out using any suitable reactor configuration. Non-limiting examples of suitable reactor configurations include a fixed catalyst bed, fluidized catalyst bed, moving bed, slurry bed, counter current, and transfer flow catalyst bed. A fixed catalyst bed is preferred.

[0013] The catalyst used in the hydrofining stage to remove sulfur, and nitrogen typically comprises a hydrogenation metal on a suitable catalyst support. The support may be a refractory metal oxide, for example, alumina, silica or silica-alumina. The hydrogenation metal comprises at least one metal selected from Group 6 and Groups 8-10 of the Periodic Table (based on the IUPAC Periodic Table format having Groups from 1 to 18). The metal will generally be present in the catalyst composition in the form of an oxide or sulfide. Particularly suitable metals are iron, cobalt, nickel, tungsten, molybdenum, chromium and platinum. Cobalt, nickel, molybdenum and

tungsten are the more preferred. A particularly preferred catalyst composition is Al_2O_3 promoted by CoO or NiO and MoO_3.

[0014] Any suitable effective reaction time between the catalyst composition and the feedstock may be utilized. In general, the effective reaction time will range from 0.1 hours to 10 hours. Preferably, the reaction time will range from 0.3 to 5 hours. This typically requires a liquid hourly space velocity (LHSV) in the range of 0.10 to 10 cc of oil per cc of catalyst per hour, preferably from 0.2 to 3.0 cc/cc/hr.

[0015] The temperature in the first stage will typically be in the range of 150°C to 450°C, preferably 300 to 375°C. As previously stated, the first stage is effectuated in the presence of hydrogen. Any suitable hydrogen pressure may be utilized in the hydrofining stage. The reaction pressure will generally be in the range of atmospheric to 10,000 psig (68,950 kPa). Preferably, the pressure will be in the range of 500 to 3,000 psig (3548 to 20651 kPa), more preferably 1000 to 2000 psig (6996 to 13891 kPa). The quantity of hydrogen used to contact the feed stock will generally be in the range of 100 to 10,000 standard cubic feet per barrel of the feed stream (17.8 to 1780 m^3/m^3), preferably 300 to 5,000 standard cubic feet per barrel (53.4 to 890.5 m^3/m^3), more preferably 500 to 3500 standard cubic feet per barrel (89.1 to 623.4 m^3/m^3).

[0016] As previously stated, the hydrofining stage, removes at least a portion of the sulfur heteroatoms and nitrogen heteroatom compounds present in the feedstock. By at least a portion, it is meant that the at least 50 vol.% of the sulfur heteroatom compounds are removed, preferably more than 75 vol.%, more preferably more than 90 vol.%. Typically, more than 20 vol.% of the nitrogen heteroatom compounds are removed, preferably more than 30 vol.%, and more preferably 40 vol.%. The hydrofining stage also results in the saturation of at least a portion of the aromatics present in the feedstock. By at least a portion it is meant that less than 20 vol.% of the aromatics present in the feedstock are saturated, preferably less than 15 vol.%, more preferably less than 10 vol.%, and most preferably 5 to 10 vol.% of the aromatics are saturated.

[0017] After exiting the hydrofining stage, the first stage effluent is stripped to remove at least a portion of any light hydrocarbon components and at least a portion of any hydrogen sulfide present. The stripping column used in stripping the first stage effluent can be any stripping column known in the art suitable for the above-mentioned purpose. It is preferred that the stripper used possesses a reflux tray and a feed tray. The stripping medium or manner of contacting the first stage effluent with the stripping medium is not critical to the instant invention and may be any medium or contacting manner known to be effective

in stripping operations. During the stripping operation, an intermediate stream is removed from the stripper. The intermediate stream is removed from the separator at a location wherein the intermediate stream has an API gravity (60/60°F) of 15 to 30, preferably 20 to 30, and more preferably 22 to 27. The intermediate stream is further characterized by a viscosity of 5 to 20 cSt at 40°F, preferably 10 to 20, and more preferably 10 to 15, and a viscosity index ("VI") of -25 to 5, preferably -20 to 0, and more preferably -20 to -5. The intermediate stream has a 5%LV, as determined by ASTM D6417, of 350 to 450°F, preferably 350 to 425°F, more preferably 380 to 405°F, and a 95%LV, as determined by ASTM D6417, of 700 to 1250°F, preferably 800 to 1200°F, more preferably 800 to 1000°F. The intermediate stream also contains less than 500wppm sulfur, preferably less than 400wppm, more preferably less than 300wppm. The intermediate stream is further characterized as having an aniline point of less than 200°F, preferably 100 to 200°F, more preferably 125 to 200°F, and most preferably 130 to 160°F. In the preferred embodiment, the intermediate stream is removed from the stripper at a point between the reflux tray and the feed tray.

[0018] As previously stated, the intermediate stream is passed to a catalytic dewaxing stage, sometimes referred to herein as the second stage or zone, wherein at least one second stage effluent is produced. The dewaxing catalyst

may be either crystalline or amorphous. The crystalline materials used herein are preferably molecular sieves that contain at least one 10 or 12 ring channel and may be based on aluminosilicates (zeolites) or on silicoaluminophosphates (SAPOs). Non-limiting examples of suitable zeolites include ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, ferrierite, ITQ-13, MCM-68 and MCM-71. Non-limiting examples of aluminophosphates containing at least one 10-ring channel include ECR-42. Non-limiting examples of molecular sieves containing 12 ring channels include zeolite beta, and MCM-68. The molecular sieves are described in US Patent Numbers 5,246,566, 5,282,958, 4,975,177, 4,397,827, 4,585,747, 5,075,269 and 4,440,871. MCM-68 is described in US Patent No. 6,310,265. MCM-71 and ITQ-13 are described in PCT published applications WO 0242207 and WO 0078677, all of which are incorporated herein by reference. ECR-42 is disclosed in US 6,303,534, which is also incorporated herein by reference. Preferred catalysts include ZSM-48, ZSM-22 and ZSM-23. Especially preferred is ZSM-48. The molecular sieves are preferably in the hydrogen form. Reduction can occur in situ during the dewaxing step itself or can occur ex situ in another vessel. Further, the dewaxing catalyst may be used in sulfided or unsulfided form, and is preferably in the sulfided form.

[0019] Amorphous dewaxing catalysts include alumina, fluorided alumina, silica-alumina, fluorided silica-alumina and silica-alumina doped with Group 3

metals. Such catalysts are described in, for example, US Patent Nos. 4,900,707 and 6,383,366, both of which are incorporated herein by reference.

[0020] The dewaxing catalysts used are bifunctional. By bifunctional it is meant that the dewaxing catalysts have a dewaxing function and a hydrogenation function. The hydrogenation function is preferably provided by at least one Group 6 metal, at least one Group 8 - 10 metal, or mixtures thereof. Preferred metals are Groups 9 -10 metals. Especially preferred are Groups 9 - 10 noble metals such as Pt, Pd or mixtures thereof (based on the IUPAC Periodic Table format having Groups from 1 to 18). These metals are present in an amount ranging from 0.1 to 30 wt.%, preferably 0.1 to 10 wt.%, more preferably 0.1 to 5 wt.%, based on the total weight of the catalyst. Catalyst preparation and metal loading methods are described for example in US Patent No. 6,294,077, which is incorporated herein by reference, and include, for example, ion exchange and impregnation using decomposable metal salts. Metal dispersion techniques and catalyst particle size control are described in US Patent No. 5,282,958, which is also incorporated herein by reference. Catalysts with small particle size and well-dispersed metals are preferred.

[0021] The molecular sieves are typically composited with binder materials which are usually refractory materials that are resistant to high temperatures

which may be employed under dewaxing conditions to form a finished dewaxing catalyst or may be binderless (self bound or bulk). The binder materials are typically selected from inorganic oxides such as silica, alumina, silica-aluminas, binary combinations of silicas with other metal oxides such as titania, magnesia, thoria, zirconia and the like and tertiary combinations of these oxides such as silica-alumina -thoria and silica-alumina magnesia. The amount of molecular sieve in the finished dewaxing catalyst is typically from 10 to 100 wt.%, preferably 35 to 100 wt.%, based on the total weight of the catalyst. Such catalysts are formed by methods such as, for example, spray drying, extrusion and the like.

[0022] Dewaxing conditions typically include temperatures of from 250 - 400°C, preferably 275 to 350°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), preferably 1480 to 17339 kPa (200 to 2500 psig). Typically, liquid hourly space velocities range from 0.1 to 10 hr^{-1}, preferably 0.1 to 5 hr^{-1}, and hydrogen treat gas rates range from 45 to 1780 m^3/m^3 (250 to 10000 scf/B), preferably 89 to 890 m^3/m^3 (500 to 5000 scf/B).

[0023] The at least one second stage effluent exiting the dewaxing stage is passed to a hydrotreating stage, sometimes referred to herein as the third zone or stage. In some instances, it may be preferred to utilize a cooling stage between

the dewaxing stage. The cooling stage allows the practitioner to operate the dewaxing stage at high temperatures. Interstage cooling can be effectuated through the use of any means known to effectively lower the temperature of a process stream. Non-limiting examples include direct and indirect heat exchangers.

[0024] The term "hydrotreating" as used herein refers to processes wherein a hydrogen-containing treat gas is used in the presence of a suitable hydrotreating catalyst that is primarily active for the removal of heteroatoms, such as sulfur, and nitrogen. Suitable hydrotreating catalysts for use in the present invention are any conventional hydrotreating catalyst and includes those which are comprised of at least one Group 8-10 metal, preferably Fe, Co and Ni, more preferably Co and/or Ni, and most preferably Co; and at least one Group 6 or 16 metal, preferably Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. It is within the scope of the present invention that more than one type of hydrotreating catalyst be used in the same reaction vessel. The Group 8-10 metal is typically present in an amount ranging from 2 to 20 wt.%, preferably from 4 to 12%. The Group 6 or 16 metal will typically be present in an amount ranging from 5 to 50 wt.%, preferably from 10 to 40 wt.%, and more preferably from 20 to 30 wt.%. All metals weight percents are on support. By "on support" we mean that the percents are based on the weight of

the support. For example, if the support were to weigh 100 g. then 20 wt.% Group 8-10 metal would mean that 20 g. of Group 8-10 metal was on the support. Typical hydrotreating temperatures range from 100°C to 400°C with pressures from 50 psig to 3,000 psig, preferably from 50 psig to 2,500 psig.

[0025] The hydrotreating of the second stage effluent produces at least one third stage effluent having a reduced amount of heteroatom species. The third stage effluent may be passed directly to a fractionation tower or it may be stripped to remove hydrogen sulfide and lighter hydrocarbon components such as light fuel oil, etc. It is preferred that the third stage effluent also be stripped. The stripping column used in stripping the third stage effluent can be any stripping column known. The stripping medium or manner of contacting the stripping medium with the third stage effluent is not critical to the instant invention and may be any medium or contacting manner known to be effective in stripping operations.

[0026] The third stage effluent is passed to a fractionating stage to produce at least one naphthenic base oil having a low aniline point. By low aniline point, it is meant that the at least one naphthenic base oil has an aniline point lower than 250°F, preferably 100 to 250°F, more preferably 100 to 200°F, more preferably 100 to 180°F. The fractionating stage employs a fractionation tower that can be

an atmospheric fractionation tower or a vacuum fractionation tower. Preferably the fractionation tower is a vacuum fractionation unit. The at least one naphthenic base oil produced by fractionating the third stage effluent typically has a viscosity of 60 SSU at 100°F to 2000 SSU at 100°F. Preferably there are at least two naphthenic base oils produced by fractionating the third stage effluent. The first naphthenic base oil has a viscosity of 100 to 750 SSU at 100°F, and the second naphthenic base oil has a viscosity greater than 750 SSU at 100°F. More preferably there are at least three naphthenic base oils produced by fractionating the third stage effluent. The first of the three naphthenic base oils has a viscosity of 100 SSU to 150 SSU at 100°F, preferably 100 to 125 SSU at 100°F. The second of the three naphthenic base oils has a viscosity of 700 to 800 SSU at 100°F, preferably 725 to 775 SSU at 100°F. The third of the three naphthenic base oils has a viscosity of 1100 to 1300 SSU at 100°F, preferably 1150 to 1250 SSU at 100°F. The fractionation of the third stage effluent also typically results in the production of a bottoms fraction having a viscosity and boiling point greater than any of the naphthenic base oil produced, and a lighter fraction typically boiling in the kerosene range.

[0027] The base oils produced by the instant invention can be used as blend components to replace lube products in the desired viscosity range. The above description is directed at preferred embodiments of the present invention and it is

not intended to limit the invention thereto. One having ordinary skill in the art will recognize that there are modifications and variations that are still within the spirit and scope of the present invention. The inventors herein contemplate any such variations and modifications and contemplate to cover such variations and modifications within the true spirit and scope of the present invention with the attached claims.

CLAIMS:

1. A process to produce at least one naphthenic base oil having a low aniline point from a hydrocarbon feedstock containing heteroatom species and aromatics and boiling in the gas oil range, said process comprising:

a) hydrofining said feedstock under hydrofining conditions effective for removing at least a portion of the heteroatom species and saturating at least a portion of said aromatics to produce a first stage effluent having a reduced amount of heteroatom species;

b) stripping said first stage effluent in a stripping column wherein at least one intermediate stream is removed from said stripping column;

c) dewaxing said intermediate stream under catalytic dewaxing conditions to produce at least one second stage effluent containing heteroatom species;

d) hydrotreating said second stage effluent under hydrotreating conditions effective for removing at least a portion of the heteroatom species to produce at least one third stage effluent having a reduced amount of heteroatom species; and

e) fractionating said third stage effluent to produce at least one base oil.

2. The process according to claim 1 wherein said feedstock is a mixture of several less desirable refinery streams such as, for example, coker gas oil, lube extracts, deasphalted oil, fuels distillates, and cracker resids.

3. The process according to claim 2 wherein said catalytic dewaxing conditions include temperatures from 250 - 400°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), liquid hourly space velocities ranging from 0.1 to 10 hr^{-1}, and hydrogen treat gas rates range from 45 to 1780 m^3/m^3 (250 to 10000 scf/B).

4. The process according to claim 3 wherein catalysts used in dewaxing said intermediate stream are selected from 10 or 12 ring zeolites and silicoaluminophosphates.

5. The process according to claim 3 wherein said hydrotreating conditions include temperatures from 100°C to 400°C and pressures from 50 psig to 3,000 psig.

6. The process according to claim 5 wherein catalysts used in hydrotreating said second stage effluent are selected from conventional hydrotreating catalysts comprising 2 to 20 wt.% of at least one metal selected from Group 8-10 metals,

and 5 to 50 wt.% of at least one Group 6 or 16 metal on a high surface area support material.

7. The process according to claim 6 wherein said intermediate stream has an API gravity (60/60°F) of 15 to 30, a viscosity of 5 to 20 cSt at 40°F, a viscosity index ("VI") of -25 to 5, a 5%LV of 350 to 450°F, and a 95%LV of 700 to 1250°F.

8. The process according to claim 7 wherein said intermediate stream is further characterized as having less than 500wppm sulfur, and an aniline point of less than 200°F.

9. The process according to claim 6 wherein said intermediate stream has an API gravity (60/60°F) of 20 to 30, a viscosity of 10 to 20 at 40°F, a viscosity index ("VI") of -20 to 0, a 5%LV of 350 to 425°F, and a 95%LV of 800 to 1200°F.

10. The process according to claim 7 wherein said intermediate stream is further characterized as having less than 400wppm sulfur, and an aniline point of 125 to 200°F.

11. The process according to claim 6 wherein said intermediate stream API gravity (60/60°F) of 22 to 27, a viscosity of 10 to 15 at 40°F, a viscosity index ("VI") of -20 to -5, a 5%LV of 380 to 405°F, and a 95%LV of 800 to 1000°F.

12. The process according to claim 7 wherein said intermediate stream is further characterized as having less than 300wppm sulfur, and an aniline point of 130 to 160°F.

13. The process according to claim 9 wherein fractionating said third stage effluent to produces at least two base oils.

14. The process according to claim 11 wherein fractionating said third stage effluent to produces at least three base oils, a fraction boiling higher than any of said three base oils and a fraction boiling in the kerosene range.

15. The process according to claim 2 wherein said at least one base oil has a viscosity of 60 SSU to 2000 SSU at 100°F.

16. The process according to claim 13 wherein the first of said at least two base oils has a viscosity of 100 SSU to 750 SSU at 100°F, and the second of said at least two base oils has a viscosity greater than 750 SSU at 100°F.

17. The process according to claim 14 wherein the first of said at least three base oils has a viscosity of 100 SSU to 150 SSU at 100°F; the second of said at least two base oils has a viscosity of greater than 700 SSU to 800 SSU at 100°F, and the third of said at least three base oils has a viscosity of 1100 SSU to 1300 SSU at 100°F.