

A PROCESS FOR MAKING LUBE OIL BASESTOCKS

FIELD OF THE INVENTION

[0001] This invention relates to a process for preparing lubricating oil basestocks from lube oil boiling range feedstreams. More particularly, the present invention is directed at a process wherein a wax containing feedstock is hydrotreated over a stacked bed catalyst system thereby producing a lube oil boiling range basestock.

BACKGROUND OF THE INVENTION

[0002] It has long been recognized that one of the most valuable products generated through the refining of crude mineral oils is lubricating oils. It is common practice to recover lubricating oil basestocks by solvent extracting, with a selective solvent, undesirable components such as sulfur compounds, oxygenated compounds, and aromatics from straight distillates. However, with the decline in the availability of paraffinic base crudes, and a corresponding increase in the proportion of naphthenic and asphaltic base crudes, it is becoming increasingly difficult to meet the demand for lubricating oil basestocks, or base oils. For example, American Petroleum Institute (API) requirements for Group II basestocks include a saturates content of at least 90%, a sulfur content of 0.03 wt.% or less and a viscosity index (VI) between 80 and 120. Thus, there is a trend in the lube oil market to use Group II basestocks instead of Group I basestocks in order to meet the demand for higher quality basestocks that provide for increased fuel economy, reduced emissions, etc.

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[0003] Conventional techniques for preparing basestocks such as hydrocracking or solvent extraction require severe operating conditions such as high pressure and temperature or high solvent:oil ratios and high extraction temperatures to reach these higher basestock qualities. Either alternative involves expensive operating conditions and low yields.

[0004] Hydrocracking has been combined with hydrotreating as a preliminary step. However, this combination also results in decreased yields of lubricating oils due to the conversion to distillates that typically accompany the hydrocracking process.

[0005] Thus, as the demand for quality lube oil basestock continues to increase, the search for new and different processes, catalysts, and catalyst systems that exhibit improved activity, increased yields, selectivity and/or longevity is a continuous, ongoing exercise. Therefore, there is a need in the lube oil market to provide processes that can produce lube oil basestocks that meet the demand for increased fuel economy, reduced emissions, etc.

BRIEF DESCRIPTION OF THE FIGURE

[0006] The Figure is a plot of the relative volume activity of various catalysts and catalyst systems versus the days the respective catalysts and catalyst systems were on stream.

SUMMARY OF THE INVENTION

[0007] The present invention is directed at a process to prepare lubricating oil basestocks from lube oil boiling range feedstocks. The process comprises:

- a) contacting a lube oil boiling range feedstock with a stacked bed hydrotreating catalyst system in a reaction stage operated under effective conditions thereby producing a hydrotreated effluent comprising at least a gaseous product and a hydrotreated lubricating oil boiling range feedstock; and
- b) stripping the hydrotreated effluent to remove at least a portion of the gaseous product from the hydrotreated effluent thereby producing at least a lubricating oil basestock.

[0008] In one embodiment of the instant invention, the stacked bed hydrotreating catalyst system comprises a first and second catalyst, the first catalyst comprising a conventional hydrotreating catalyst having an average pore diameter of greater than 10 nm and said second catalyst comprises a bulk metal hydrotreating catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0009] It should be noted that the terms "feedstock" and "feedstream" as used herein are synonymous.

[0010] The present process involves hydrotreating a lubricating oil feedstock with a stacked bed hydrotreating catalyst system in a reaction stage operated under effective hydrotreating conditions to produce a hydrotreated effluent comprising at least a gaseous product and a hydrotreated lubricating oil feedstock. The

hydrotreated effluent is stripped to remove at least a portion of the gaseous product from the hydrotreated effluent thereby producing at least a lubricating oil basestock. Lube oil basestocks having a saturates content of at least 90%, a sulfur content of 0.03 wt.% or less, and a viscosity index (VI) between 80 and 120 can readily be produced through the use of the instant invention.

Lubricating Oil Feedstocks

[0011] Feedstocks suitable for use in the present invention are wax-containing feeds that boil in the lubricating oil range, typically having a 10% distillation point greater than 650°F (343°C) and an endpoint greater than 800°F (426°C), measured by ASTM D 86 or ASTM 2887. These feedstocks can be derived from mineral sources, synthetic sources, or a mixture of the two. Non-limiting examples of suitable lubricating oil feedstocks include those derived from sources such as oils derived from solvent refining processes such as raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, dewaxed oils, automatic transmission fluid feedstocks, and Fischer-Tropsch waxes. Automatic transmission fluid ("ATF") feedstocks are lube oil feedstocks having an initial boiling point between 200°C and 275°C, and a 10% distillation point greater than 300°C. ATF feedstocks are typically 75-110N feedstocks.

[0012] These feedstocks may also have high contents of nitrogen- and sulfur-contaminants. Feeds containing up to 0.2 wt.% of nitrogen, based on feed and up to 3.0 wt.% of sulfur can be processed in the present process. Feeds having a high wax content typically have high viscosity indexes of up to 200 or more. Sulfur and nitrogen contents may be measured by standard ASTM methods D5453 and D4629, respectively.

Hydrotreating

[0013] It should be noted that the term "hydrotreating" as used herein refers to processes wherein a hydrogen-containing treat gas is used in the presence of a suitable catalyst that is primarily active for the removal of heteroatoms, such as sulfur, and nitrogen, and saturation of aromatics. In the practice of the present invention, the lubricating oil feedstock is hydrotreated with a stacked bed hydrotreating catalyst system in a reaction stage operated under effective hydrotreating conditions to produce a hydrotreated effluent comprising at least a gaseous product and a hydrotreated lubricating oil feedstock.

[0014] The catalyst system used herein comprises at least a first and second hydrotreating catalyst. By "stacked bed" it is meant that the first catalyst appears in a separate catalyst bed, reactor, or reaction zone, and the second hydrotreating catalyst appears in a separate catalyst bed, reactor, or reaction zone downstream, in relation to the flow of the lubricating oil feedstock, from the first catalyst.

[0015] The first hydrotreating catalyst is a supported catalyst. Suitable hydrotreating catalysts for use as the first catalyst of the present catalyst system include any conventional hydrotreating catalyst. Conventional hydrotreating catalyst as used herein is meant to refer to those which are comprised of at least one Group VIII metal, preferably Fe, Co and Ni, more preferably Co and/or Ni, and most preferably Ni; and at least one Group VI metal, preferably Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. The Group VIII metal is typically present in an amount ranging from 2 to 20 wt.%, preferably from 4 to 12%. The Group VI 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 VIII metal would mean that 20 g. of Group VIII metal was on the support.

[0016] However, not all conventional hydrotreating catalysts fitting the above-described criteria are suitable for use in the present invention. The inventors hereof have unexpectedly found that the average pore diameter of the first catalyst must have a specific size to be suitable for use herein. Thus, in the practice of the present invention, a conventional catalyst, as described above, but having an average pore diameter greater than 10nm, as measured by water adsorption porosimetry, must be used as the first catalyst of the present stacked bed catalyst system. It is preferred that the average pore diameter of the first catalyst, i.e. the conventional hydrotreating catalyst, of the present stacked bed catalyst system be greater than 11nm, more preferably greater than 12nm.

[0017] The second hydrotreating catalyst is a bulk metal catalyst. By bulk metal, it is meant that the catalysts are unsupported wherein the bulk catalyst particles comprise 30 - 100 wt.% of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the bulk catalyst particles, calculated as metal oxides and wherein the bulk catalyst particles have a surface area of at least 10 m²/g. It is furthermore preferred that the bulk metal hydrotreating catalysts used herein comprise 50 to 100 wt.%, and even more preferably 70 to 100 wt.%, of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the particles, calculated as metal oxides. The amount of Group VIB and Group VIII non-noble metals can easily be determined VIB TEM-EDX.

[0018] Bulk catalyst compositions comprising one Group VIII non-noble metal and two Group VIB metals are preferred. It has been found that in this case, the bulk catalyst particles are sintering-resistant. Thus the active surface area of the bulk catalyst particles is maintained during use. The molar ratio of Group VIB to Group VIII non-noble metals ranges generally from 10:1 - 1:10 and preferably from 3:1 - 1:3. In the case of a core-shell structured particle, these ratios of course apply to the metals contained in the shell. If more than one Group VIB metal is contained in the bulk catalyst particles, the ratio of the different Group VIB metals is generally not critical. The same holds when more than one Group VIII non-noble metal is applied. In the case where molybdenum and tungsten are present as Group VIB metals, the molybdenum:tungsten ratio preferably lies in the range of 9:1 - 1:9. Preferably the Group VIII non-noble metal comprises nickel and/or cobalt. It is further preferred that the Group VIB metal comprises a combination of molybdenum and tungsten. Preferably, combinations of nickel/molybdenum/tungsten and cobalt/molybdenum/tungsten and nickel/cobalt/molybdenum/tungsten are used. These types of precipitates appear to be sinter-resistant. Thus, the active surface area of the precipitate is remained during use. The metals are preferably present as oxidic compounds of the corresponding metals, or if the catalyst composition has been sulfided, sulfidic compounds of the corresponding metals.

[0019] It is also preferred that the bulk metal hydrotreating catalysts used herein have a surface area of at least 50 m²/g and more preferably of at least 100 m²/g. It is also desired that the pore size distribution of the bulk metal hydrotreating catalysts be approximately the same as the one of conventional hydrotreating catalysts. More in particular, these bulk metal hydrotreating catalysts have

preferably a pore volume of 0.05 - 5 ml/g, more preferably of 0.1 - 4 ml/g, still more preferably of 0.1 - 3 ml/g and most preferably 0.1 - 2 ml/g determined by nitrogen adsorption. Preferably, pores smaller than 1 nm are not present. Furthermore these bulk metal hydrotreating catalysts preferably have a median diameter of at least 50 nm, more preferably at least 100 nm, and preferably not more than 5000 μm and more preferably not more than 3000 μm . Even more preferably, the median particle diameter lies in the range of 0.1 - 50 μm and most preferably in the range of 0.5 - 50 μm .

[0020] The reaction stage containing the stacked bed hydrotreating catalyst system used in the present invention can be comprised of one or more fixed bed reactors or reaction zones each of which can comprise one or more catalyst beds of the same or different catalyst. Although other types of catalyst beds can be used, fixed beds are preferred. Such other types of catalyst beds include fluidized beds, ebullating beds, slurry beds, and moving beds. Interstage cooling or heating between reactors, reaction zones, or between catalyst beds in the same reactor, can be employed since some olefin saturation can take place, and olefin saturation and the desulfurization reaction are generally exothermic. A portion of the heat generated during hydrotreating can be recovered. Where this heat recovery option is not available, conventional cooling may be performed through cooling utilities such as cooling water or air, or through use of a hydrogen quench stream. In this manner, optimum reaction temperatures can be more easily maintained.

[0021] The catalyst system of the present invention comprises 5-95 vol.% of the first catalyst with the second catalyst comprising the remainder, preferably 40-60 vol.%, more preferably 5 to 50 vol.%. Thus, if the catalyst system comprises 50 vol.% of the first catalyst, the second catalyst will comprise 50 vol.% also.

[0022] Effective hydrotreating conditions include temperatures of from 150 to 400°C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), a space velocity of from 0.1 to 10 liquid hourly space velocity (LHSV), and a hydrogen to feed ratio of from 89 to 1780 m³/m³ (500 to 10000 scf/B).

[0023] As stated above, the contacting of the lube oil boiling range feedstock with the stacked bed hydrotreating catalyst system produces a hydrotreated effluent comprising at least a gaseous product and a hydrotreated lubricating oil feedstock. The hydrotreated effluent is stripped to remove at least a portion of the gaseous product from the hydrotreated effluent thereby producing at least a lubricating oil basestock. The means used herein to strip the hydrotreated effluent is not critical to the present invention. Thus, any stripping method, process, or means known can be used. Non-limiting examples of suitable stripping methods, means, and processes include flash drums, fractionators, knock-out drums, steam stripping, etc.

[0024] The above description is directed to preferred embodiments of the present invention. Those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0025] The following examples will illustrate the improved effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

EXAMPLES**EXAMPLE 1**

[0026] A medium vacuum gas oil having the properties outlined in Table 1 was processed in an isothermal pilot plant over three catalysts systems at 1200 psig hydrogen partial pressure. The catalyst systems and operating conditions are given in Table 2. Catalyst B is a conventional hydrotreating catalyst having 4.5 wt.% Group VI metal, 23 wt.% Group VIII metal on an alumina support and has an average pore size of 14.0 nm. The bulk metal hydrotreating catalyst was a commercial bulk metal hydrotreating catalyst marketed under the name Nebula by Akzo-Nobel.

[0027] In the Examples, all the catalyst systems were lined out at 50 days on stream. A first order kinetic model with an activation energy of 31,000 cal/gmol was used to compare volume activities between the catalysts.

TABLE 1

	Medium Vacuum Gas Oil
Density at 70°C (g/cc)	0.88
Nitrogen (wppm)	700
Sulfur (wt.%)	2.6
GCD 5 WT% Boiling Point (°C)	334
GCD 50 WT% Boiling Point (°C)	441
GCD 95 WT% Boiling Point (°C)	531

TABLE 2

Catalyst System	100 vol.% Catalyst B	100 vol.% Nebula 1	50 vol.% Catalyst B followed by 50 vol.% Nebula 1
Average Catalyst Temperature (°C)	370	380	370
Liquid Hourly Space Velocity (hr ⁻¹)	2	1	1
Stripped reactor Effluent Nitrogen Content (wppm)	227	17	34
Nitrogen Removal Relative Volume Activity	1	1.18	1.34

[0028] The Nitrogen Removal Relative Volume Activity ("RVA") for each catalyst system was calculated by simple first order kinetic modeling. As shown in Table 2, the 50/50 vol.% stacked bed catalyst system, with the large average pore size Catalyst B upstream of the bulk metal catalyst, showed higher nitrogen removal activity than either of the single catalyst systems demonstrated on their own.

EXAMPLE 2

[0029] The hydrotreating ability of different stacked beds of Catalyst B and Nebula were analyzed by hydrotreating different feedstreams over the stacked beds in the in two parallel reactor trains of the same isothermal pilot plant unit used in Example 1 above. The feedstreams used were Medium Cycle Oils("MCO") from an FCC unit and blends of the MCO with a virgin feedstock were tested in two parallel reactor trains. The feed properties are described in Table 3, below.

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[0030] In this Example, one reactor train consisted entirely of a conventional NiMo on Alumina hydrotreating catalyst, Catalyst C, with an average pore diameter of 7.5 nm. The other reactor train contained a stacked bed system with 75-vol. % of Catalyst C followed by 25-vol. % of Catalyst A, a bulk multimetallic sulfide catalyst having an average pore diameter of 5.5 nm.

[0031] The separate reactors in both trains were immersed in a fluidized sandbath for efficient heat transfer. Thus, the temperature of the first 75-vol. % of Catalyst C was at the same temperature whether it was in train 1 or 2. Likewise, the last 25-vol. % of Catalyst C in train 1 was at the same temperature as the last 25-vol. % of Catalyst A in train 2. Therefore, In Example 2, each of the two reactor trains was divided into two separate reactor vessels where the temperature of the first 75-volume% containing 75 vol.% of the catalyst loading of that reactor could be independently controlled from the last 25-volume % of catalyst.

[0032] The operating conditions for the two trains were 1350 psig H₂, liquid hourly space velocities ("LHSV") of 1.4 vol./hr/vol., and 5500-6300 SCF/B of hydrogen. The temperature schedule for both trains is described in Table 4 below.

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TABLE 3

<u>FEED</u>	<u>50% Normal FCC MCO</u>	<u>67% Normal FCC MCO</u>	<u>100% Normal FCC MCO</u>	<u>100% Heavy FCC MCO</u>
API Gravity	18.1	15.0	9.5	7.0
Hydrogen, wt. %	10.65	10.04	8.77	8.61
Sulfur, wt. %	3.23	3.53	4.28	4.40
Nitrogen, ppm	959	1153	1485	1573
Aromatics-Mono, wt. %	-	-	12.0	8.8
Aromatics-Di, wt. %	-	-	43.9	41.7
Aromatics-Poly, wt. %	-	-	22.4	30.7
Distillation, D2887 GCD				
10	498	493	485	493
50	627	625	618	642
90	703	705	706	749
95	726	721	724	777

TABLE 4

<u>Days on Oil</u>	<u>Feedstock</u>	<u>75%/25% Temperatures, °F</u>
4-6	50% FCC MCO	585/650
7-15	67% FCC MCO	585/650
16-30	100% FCC MCO	585-610/650-675
31-50	100% Heavy FCC MCO	610-635/675-700

[0033] The relative HDN volume activity of the stacked bed Catalyst C/Catalyst A compared to Catalyst A is shown in the figure below. Note that for the 50%, 67% and 100% FCC MCO feeds the stacked bed system with only 25-volume % of Catalyst A shows a stable activity advantage of 275%.

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[0034] As shown in the Figure, when the 100% Heavy FCC MCO was used as the feed note the activity advantage for the stacked bed catalyst system containing begins to decrease from 275% to 225% and then was subsequently reduced over 20 days to slightly less than 150%.

EXAMPLE 3

[0035] In this Example, a stacked bed catalyst system containing 75 vol.% of Catalyst B and 25 vol.% Nebula, both as described above, was used to hydrotreat a light cycle cat oil feed ("Feed A") and a heavier medium cycle cat oil feed ("Feed B") as described in Table 5 below. Example 2 was conducted in the same two reactor train pilot plant unit as described in Example 2 above. The operating conditions for the two trains were 1200 psig H₂, liquid hourly space velocities of 2 vol./hr/vol., and 5000 SCF/B of hydrogen.

[0036] The reactor effluents were stripped with nitrogen in an oven at 100°C to remove substantially all of the gaseous reaction products. The nitrogen content of the liquid reactor effluent was then analyzed by ASTM 4629. The temperature schedules for both trains along with the results of this example are described in Table 5 below.

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TABLE 5

<u>FEED</u>	<u>Feed A</u>	<u>Feed B</u>
API Gravity	0.973	0.9
Sulfur, wt. %	2.6	2.50
Nitrogen, ppm	713	742
Distillation, D2887 GCD		
5	427	448
50	551	590
95	707	755
EP	764	823
Catalyst B Temperature	570	617
Nebula Temperature	645	692
Stripped Reactor Effluent		
Nitrogen Content	2	7
Nitrogen Removal Relative		
Volume Activity	1.75	1.75

[0037] As can be seen in Table 5, when a conventional catalyst having an average pore diameter of 14nm was used in the first 75 vol.% of the reactor, the Nitrogen Removal Relative Volume Activity ("RVA") for the catalyst system remained constant when the heavier feed was used. In comparing the results of Example 3 to those obtained in Example 2, one can see that when a catalyst having a pore volume of 7.5nm preceded the bulk metal catalyst, the RVA of the catalyst system decreased. However, in Example 3, the heavier feed did not negatively impact the RVA of the catalyst system.

CLAIMS:

1. A process to prepare lubricating oil basestocks from a lube oil boiling range feedstock comprising:

- a) contacting a lube oil boiling range feedstock with a stacked bed hydrotreating catalyst system comprising at least a first and second hydrotreating catalyst in a reaction stage operated under effective hydrotreating conditions thereby producing a hydrotreated effluent comprising at least a gaseous product and a hydrotreated lubricating oil boiling range feedstock; and
- b) stripping the hydrotreated effluent to remove at least a portion of the gaseous product from the hydrotreated effluent thereby producing at least a lubricating oil basestock;

wherein said first hydrotreating catalyst is selected from supported hydrotreating catalysts comprising 2 to 20 wt.% of at least one Group VIII metal, and 5 to 50 wt.% of at least one Group VI metal on a high surface area support material having an average pore diameter of greater than 10nm and said second hydrotreating catalyst is selected from bulk metal hydrotreating catalyst comprising 30 to 100 wt.% of at least one Group VIII non-noble metal and at least one Group VIB metal, based on the total weight of the bulk catalyst particles, calculated as metal oxides and wherein the bulk catalyst particles have a surface area of at least 10 m²/g.

2. The process according to claim 1 wherein said lubricating oil feedstock has a 10% distillation point greater than 650°F (343°C) and an endpoint of greater than 800°F (426°C), measured by ASTM D 86 or ASTM 2887, and are derived from mineral sources, synthetic sources, or a mixture of the two.

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3. The process according to any of the preceding claims wherein said lubricating oil feedstock is selected from those derived from sources such as oils derived from solvent refining processes such as raffinates, partially solvent dewaxed oils, deasphalted oils, distillates, vacuum gas oils, coker gas oils, slack waxes, foots oils and the like, dewaxed oils, automatic transmission fluid feedstocks, and Fischer-Tropsch waxes.
4. The process according to any of the preceding claims wherein said lubricating oil feedstock contains up to 0.2 wt.% of nitrogen, based on the lubricating oil feedstock, and up to 3.0 wt.% of sulfur, based on the lubricating oil feedstock.
5. The process according to any of the preceding claims wherein said Group VIII metal of said first hydrotreating catalyst is selected from Co Ni, and mixtures thereof, said Group VI metal of said first hydrotreating catalyst is selected from Mo, W, and mixtures thereof, and high surface area support material is selected from silica, alumina, and mixtures thereof.
6. The process according to any of the preceding claims wherein said bulk metal hydrotreating catalyst comprises one Group VIII non-noble metal and two Group VIB metals wherein the molar ratio of Group VIB to Group VIII non-noble metals ranges from 10:1 - 1:10.
7. The process according to any of the preceding claims wherein the at least one Group VIII non-noble metal and at least one Group VIB metals are present as oxidic compounds of the corresponding metals, or if the catalyst composition has been sulfided, sulfidic compounds of the corresponding metals.

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8. The process according to any of the preceding claims wherein the bulk metal hydrotreating catalysts have a surface area of at least $50 \text{ m}^2/\text{g}$, a pore size volume of 0.05 to 5 ml/g , and a median diameter of at least 50 nm .
9. The process according to any of the preceding claims wherein said effective hydrotreating conditions include temperatures of from 150 to 400°C , a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), a space velocity of from 0.1 to 10 liquid hourly space velocity (LHSV), and a hydrogen to feed ratio of from 89 to $1780 \text{ m}^3/\text{m}^3$ (500 to 10000 scf/B).
10. The process according to any of the preceding claims wherein the catalyst system of the present invention comprises 5 - $95 \text{ vol.}\%$ of the first hydrotreating catalyst with the second hydrotreating catalyst comprising the remainder.
11. The process according to any of the preceding claims wherein the catalyst system of the present invention comprises 5 - $50 \text{ vol.}\%$ of the first hydrotreating catalyst with the second hydrotreating catalyst comprising the remainder.