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(54) Process for producing a naphthenic base oil

(57) The invention is directed to a process for producing at least one naphthenic base oil from a hydrocarbon feed containing heteroatom species and aromatics, comprising the steps of:
a) hydrotreating the feed under hydrotreating conditions effective for removing at least a portion of the heteroatom species and saturating at least a portion of the aromatics to produce a first stage effluent having a reduced amount of heteroatom species; and
b) removing gaseous and liquid fractions boiling in the gas oil range from the effluent from step (a), and
c) dewaxing the effluent obtained in step (b) under catalytic dewaxing conditions in the presence of a catalyst composition comprising a molecular sieve containing covalently bound alumina moieties in its framework and having pores with a diameter in the range of from 0.35 to 0.80 nm, wherein the molecular sieve has been modified to reduce the mole percentage of alumina, to produce at least one effluent, and
d) fractionating the effluent obtained in step(c) to produce at least one naphthenic base oil grade.

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Description

[0001] The present invention relates to a process for producing a naphthenic base oil. More particularly, the invention relates to an improved process for producing naphthenic base oils in the lubricating viscosity range in increased yields from naphthenic crude oils comp rising minor amounts of wax. The present invention also relates to a catalytic dewaxing process suitable for dewaxing naphthenic hydrocarbon oils containing waxy molecules, and to the lubricating base oils obtained.

[0002] Crude petroleum sources featuring a value for the Watson characterisation factor K of in between 11 and 12 are also referred to as "naphthenic" crude oil, while below a K factor of 11, a crude oil is generally referred to as an "aromatic" crude oil. The Watson characterisation factor K for hydrocarbons has been defined in the API technical data book (Section 2 Characterisation).

[0003] Typical naphthenic crudes include for instance the African crudes, such as Forcados, Nigerian Light; FarEast crudes, such as Champion Export; Venezuelan crudes such as Tia Juana Pesado and Laguna; and Danish crudes such as DUC crude, while typical semi-naphthenic crudes include Alba.

[0004] The production of naphthenic base oils from such naphthenic base oils usually does not involve a dedicated dewaxing step, since naphthenic crude oils contain little or no wax molecules.

[0005] However, due to shortening supplies of truly naphthenic crude, so-called semi-naphthenic crude oils comprising increasing amounts of wax become more important sources for base oil and gas oil production. As a consequence, the pour points of the distillates are high, since the presence of even a small amount of wax in the crude oil increases the pour point disproportional. On the other hand, the wax molecules present in such semi-naphthenic crude oils are usually too high in molecular weight to contribute beneficially to the gas oil properties, such as the Cetane Number requirements for Automotive Gasoils, or Kerosine/Avtur smoke point specifications due to the low concentration of n- and isoparaffinic components in the appropriate boiling range.

[0006] Furthermore, the amounts of wax present are usually not high enough to permit effective removal through physical separation methods, e.g. solvent dewaxing.

[0007] US-A-4,744,884 and US-A-4,699,707 disclose a process comprising hydrotreating of a shale oil and then hydrodewaxing the effluent from the hydrotreating step. The process produces lubricant base oil fractions boiling above 343°C and having a pour point at or below -12° C and a viscosity index of at least 95. 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.

[0008] US-A-5,976,354 discloses a process to prepare a light oil and a finished oil, comprising 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.

[0009] However, both processes only deliver a limited yield of the desired base oil products.

[0010] It was found that removal of the wax molecule through conventional catalytic hydroisomerisation reduces the base oil yield through cracking, while only yielding a slightly improved gas oil yield of higher cetane number, since most wax is cracked away into the naphtha range.

[0011] Accordingly, there remains the need for a process that permits to selectively produce naphthenic base oils with low pour points from naphthenic and semi-naphthenic base oils. Furthermore, it would be desirable to also produce gas oil with acceptable properties.

[0012] This has now been achieved by the inventors, by subjecting the deasphalted and distillate fractions boiling in the base oil range to a catalytic dewaxing treatment in the presence of a highly selective catalyst, thereby yielding a dewaxed naphthenic base oil with a minimum yield and viscosity index loss.

[0013] Accordingly, the present invention relates to a process to produce at least one naphthenic base oil from a hydrocarbon feed containing heteroatom species and aromatics, comprising the steps of:

(a) hydrotreating the feed under hydrotreating conditions effective for removing at least a portion of the heteroatom species and saturating at least a portion of the aromatics to produce a first stage effluent having a reduced amount of heteroatom species; and
(b) optionally removing gaseous and liquid fractions boiling in the gas oil range from the effluent from step (a), and
(c) dewaxing the effluent from step (a) or optionally, (b) under catalytic dewaxing conditions to produce at least one effluent in the presence of a catalyst composition comprising a molecular sieve containing covalently bound alumina moieties in its framework and having pores with a diameter in the range of from 0.35 to 0.80 nm, wherein the molecular sieve has been modified to reduce the mole percentage of alumina, and
(d) fractionating the effluent from step (c) effluent to produce at least one naphthenic base oil grade.

[0014] In step (a), the feed is subjected to a hydrocracking reaction to reduce the nitrogen levels of the feeds to levels low enough so that the downstream catalytic dewaxing unit will retain its activity over a prolonged period, and at the same time to saturate polyaromatics such that the resulting products have less than 3 wt% PCA content.

[0015] The hydrocarbon feed is preferably derived from a mineral crude oil having a K value for the Watson characterisation factor of in between 11 and 12 and boiling in the base 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, or API Group I crude oil. Accordingly, the hydrocarbon feed is preferably derived from a naphthenic API Group I crude oil. More preferably, the hydrocarbon feed is a hydrotreated vacuum distillate fraction boiling between 300 and 620 °C (ASTM D2887), or a Deasphalted Oil (DAO).

[0016] Optional step (b) included between the hydrocracking and the catalytic dewaxing step allows to remove the light ends obtained in step (a) in case it could be desired to remove such light ends. This might preferably be applied if their presence would have an impact on the performance of the catalytic dewaxing step, e.g. excessive cracking, or catalyst deactivation. In addition, it advantageously allows use of a catalytic reactor of smaller dimensions. Alternatively, a hydrofinishing step may be employed after the catalytic dewaxing step. This hydrofinishing step may advantageously decrease the remaining aromatic contents, in particular of any polyaromatic compounds left in the base oil so that the base oils thus obtained will be able to meet the PCA specifications.

[0017] Prior to the catalytic dewaxing process step (c) according to the invention, the vacuum distillate fraction employed as feed or any other sulphur or nitrogen-containing feed is preferably treated to a hydrotreating step in order to reduce the concentration of sulphur and/or nitrogen in the feed. The hydrotreating step preferably involves contacting the feed with hydrogen in the presence of a suitable catalyst. Such catalysts are known in the art and in principle any hydrotreating catalyst known to be active in the hydrodesulphurisation and hydrodenitrogenation of the relevant hydrocarbon feeds may be used. Suitable catalysts, then, include those catalysts comprising as the non-noble Group VIII metal component one or more of nickel (Ni) and cobalt (Co) in an amount of from 1 to 25 percent by weight (%wt), preferably 2 to 15 %wt, calculated as element relative to total weight of catalyst and as the Group VIB metal component one or more of molybdenum (Mo) and tungsten (W) in an amount of from 5 to 30 %wt, preferably 10 to 25 %wt, calculated as element relative to total weight of catalyst. These metal components may be present in elemental, oxidic and/or sulphidic form and are supported on a refractory oxide carrier. The refractory oxide support of the first stage catalyst may be any inorganic oxide, alumino-silicate or combination of these, optionally in combination with an inert binder material. Examples of suitable refractory oxides include inorganic oxides, such as alumina, silica, titania, zirconia, boria, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these. In a preferred embodiment an acidic carrier such as alumina, silica-alumina or fluorided alumina is used as the refractory oxide carrier. The refractory oxide support may also be an aluminosilicate. Both synthetic and naturally occurring aluminosilicates may be used. Examples are natural or dealuminated zeolite beta, faujasite and zeolite Y. From a selectivity point of view it is preferred to use the dealuminated form of these zeolites. A preferred aluminosilicate to be applied is alumina-bound, at least partially dealuminated, zeolite Y.

[0018] Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, suitably from 15 to 100 bar, more suitably from 15 to 65 bar, weight hourly space velocities (WHSV) in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), suitably from 0.2 to 5 kg/l/hr, more suitably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil.

[0019] The weight ratio of the metallosilicate crystallites and the binder is between 5:95 and 35:65. Preferably the weight ratio is 10:90 and above. The upper ratio is preferably lower than 30:70. It has been found that a lower ratio is beneficial for achieving the advantages of the present invention. However when lowering this ratio a higher operating temperature is required to achieve a comparable pour point reduction. Therefore a ratio of 5:95 is the practical lower range of the metallosilicate crystallites to binder weight ratio, because at lower ratios the required operating temperatures will be too high for practical applications.

[0020] The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are: alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these binder materials are as silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

[0021] The hydrogenation component suitably comprises at least one Group VIB metal component and/or at least one Group VIII metal component. Group VIB metal components include tungsten, molybdenum and/or chromium as sulphide, oxide and/or in elemental form. If present, a Group VIB metal component is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of support, i.e. modified molecular sieve plus binder.

[0022] More preferably only a Group VIII metal component is present as the catalytically active hydrogenation component. Group VIII metal components include those components based on both noble and non-noble metals. Particularly suitable Group VIII metal components, accordingly, are palladium, platinum, nickel and/or cobalt in sulphidic, oxidic and/or elemental form. The total amount Group VIII metal will suitably not exceed 10% by weight calculated as element and based on total weight of support, and preferably is in the range of from 0.1 to 5.0% by weight, more preferably from 0.2 to 3.0% by weight. If both platinum and palladium are present, the weight ratio of platinum to palladium may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5. Catalysts comprising palladium and/or platinum as the hydrogenation component are preferred.

[0023] The metallosilicate crystallites have a crystalline microporous structure and can generally be defined as being built up of three-dimensional frameworks of tetrahedral SiO4 units and tetrahedral M units or tetrahedral SiO4 units and octahedral M units which units are corner linked via oxygen atoms. Examples of possible metals for M are Al, Fe, B, Ga or Ti or combinations of these metals. Preferred metallosilicate crystallites are aluminosilicate zeolite crystallites suitably having pores with a diameter in the range of from 0.35 to 0.80 nm. Preferred aluminosilicate zeolite crystallites include MFI-type zeolites having pores with diameters of 0.55 and 0.56 nm, such as ZSM-5 and silicalite, offretite having pores with diameters of approximately 0.68 nm and zeolites of the ferrierite group having pores with diameter of 0.54 nm, such as ZSM-35 and ferrierite. Another preferred class of aluminosilicate zeolite crystallites include TON-type zeolites. Examples of TON type aluminosilicate zeolite crystallites are ZSM-22, Theta-1 and Nu-10 as described in US-A-5336478, EP A 57049 and EP-A-65400. A further preferred class of aluminosilicate zeolite crystallites are of the MTW-type. Examples of molecular sieve crystallites having the MTW type topology are ZSM-12, Nu-13, TEA-silicate, TPZ-12, VS-12 and Theta-3 as for example described in US A-3832449, EP-A-513118, EP-A-59059 and EP-A-162719. A next preferred class of aluminosilicate zeolite crystallites are of the MTT-type. Examples of aluminosilicate zeolite crystallites having the MTT-type topology are ZSM 23, SSZ-32, ISI-4, KZ-1, and EU-13 as for example described US-A-4076842, US A 4619820, EP-A-522196, EP-A-108486 and EP-A-42226.

[0024] More preferably the zeolite crystallites have a Constraint Index of between 2 and 12. The Constraint Index is a measure of the extent to which a zeolite provides control to molecules of varying sizes to its internal structure of the zeolite. Zeolites, which provide a highly restricted access to and egress from its internal structure have a high value for the Constraint Index. On the other hand, zeolites, which provide relatively free access to the internal zeolite structure have a low value for the Constraint Index, and usually pores of large size. The method by which Constraint Index is determined is described fully in US-A-4016218, incorporated herein by reference for details of the method.

[0025] By catalytic dewaxing in step (c) is meant herein a process for decreasing the pour point of lubricating base oil products by selectively converting the components of the oil feed which impart a high pour point to products, which do not impart a high pour point. Products, which impart a high pour point are compounds having a high melting point. These compounds are referred to as waxes.

[0026] Wax compounds include for example high temperature melting normal paraffins, iso-paraffins and mono-cyclic compounds such as naphthenic compounds having alkyl side chains. The pour point is preferably reduced by at least 10 °C and more preferably by at least 20 °C. The hydrocarbon feed in the process according to the present invention will thus contain waxy molecules, which impart an undesirable high pour point. Small amounts of these compounds can strongly influence the pour point. The present process was found to be particularly suitable for the preparation of naphthenic base oils from a feed comprising between about 1% by weight and up to at most 15% by weight of these waxy compounds, more preferably of from 2 % by weight to 10 % by weight, yet more preferably from 3 % by weight to 8 % by weight of waxy compounds.

[0027] Suitable hydrocarbon feeds to be employed in the process according to the present invention are mixtures of high-boiling hydrocarbons, such as, for instance, heavy oil fractions. It has been found particularly suitable to use vacuum distillate fractions derived from an atmospheric residue, i.e. distillate fractions obtained by vacuum distillation of a residual fraction, which in return is obtained by atmospheric distillation of a crude oil, as the feed. The boiling range of such a vacuum distillate fraction is usually between 300 and 620 °C, suitably between 350 and 580 °C. Equally, deasphalted residual oil fractions, including both deasphalted atmospheric residues and deasphalted vacuum residues (deasphalted oil, also referred to as DAO), may also be employed. The present process is particularly suited for vacuum distillate fractions or DAO's containing substantial amounts of sulphur- and nitrogen-containing contaminants, for example, having sulphur levels up to 3% by weight and nitrogen levels up to 1% by weight, since these are removed in hydrodesulphurisation and hydrodenitrogenation step (a) prior to the catalytic dewaxing process according to the present invention. This is particularly suitable if a high saturates content around or above 98% by weight is desired for the resultant base oils, since the preferably a dewaxing catalyst comprising precious metal compounds is employed in step (c).

[0028] When using the above described classes of aluminosilicate zeolite crystallites, especially the zeolites of the MFI and MTW type, it has been found to be advantageous to subject the catalyst to a dealumination treatment. Advantages of this treatment are a further increase of the yield of lubricating base oil, an improved stability of the catalyst and/or an improved crush strength of the final catalyst. Dealumination results in a reduction of the number of alumina moieties present in the zeolite and hence in a reduction of the mole percentage of alumina.

[0029] Dealumination treatment is preferably performed in that the surface of the zeolite crystallites is selectively dealuminated. Surface dealumination results in a reduction of the number of surface acid sites of the zeolite crystallites, whilst not affecting the internal structure of the zeolite crystallites. The extent of dealumination of the surface of the crystallites depends on the severity of the dealumination treatment. Suitably, the number of surface acid sites of the zeolite is reduced with at least 70%, preferably with at least 80% and even more preferably with at least 90%. In a most preferred embodiment the number of surface acid sites is reduced with essentially 100% by the selective dealumination, thus leaving essentially no surface acid sites at all.

[0030] Dealumination can be attained by methods known in the art. Particularly useful methods are those, wherein the dealumination selectively occurs, or anyhow is claimed to occur selectively, at the surface of the crystallites of the molecular sieve. Examples of dealumination processes are described in WO-A-9641849. Preferably dealumination is performed by a process in which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:

$$(A)_{2/b}SiF_6$$

wherein 'A' is a metallic or non-metallic cation other than H^+ having the valence 'b'. Examples of cations 'b' are alkylammonium, NH_4^+, Mg^{++}, Li^+, Na^+, K^+, Ba^{++}, Cd^{++}, Cu^+, Ca^{++}, Cs^+, Fe^{++}, Co^{++}, Pb^{++}, Mn^{++}, Rb^+, Ag^+, Sr^{++}, Tl^+, and Zn^{++}. Preferably 'A' is the ammonium cation. The zeolite material may be contacted with the fluorosilicate salt in an amount of at least 0.0075 moles per 100 grams of the zeolite material. The pH is suitably between 3 and 7. An example of the above described dealumination process also referred to as the AHS treatment, is described in US-A-5157191.

[0031] When zeolite crystallites are used which have been subjected to a dealumination treatment the binder material is preferably a material which does not introduce acidity into the modified zeolite crystallite. Such a binder material is preferably the above described low acidity refractory oxide, which is essentially free of aluminium. It has been found that an increased mechanical strenght of the catalyst extrudate is obtained when prepared according to this sequence of steps.

[0032] Preferably small crystallites are used in order to achieve an optimum catalytic activity. Preferably crystallites smaller than 10 micron and more preferably smaller than 1 micron are used. The practical lower limit is suitably 0.01 micron. Preferably, catalysts are used having a crystallite size of between 0.05 and 0.2 μm are employed. The crystallite sized is the ultimate crystallite size, as determined by the method disclosed e.g. in Ind. Eng. Chem. Res., 1991, 30, p.12-18.

[0033] More preferably, such catalysts have been dealuminated. It has been found that the combination of small size crystallites and a surface dealumination treatment, especially the AHS treatment, as described above results in more active catalyst when compared to the same, but non-dealuminated, catalyst.

[0034] The invention is also directed to the novel catalyst compositions having such small size surface dealuminated zeolite crystallites and low acidity binder materials and their use in hydrocarbon conversion processes, optionally also comprising a Group VIII or Group VIB metal of which examples are mentioned above. Suitable processes are catalytic dewaxing, hydroisomerisation and hydrocracking.

[0035] A disadvantage of a catalyst composition having a low content of metallosilicate crystallites is that the crush strength is not always high enough to suit practical application. To overcome this problem applicants have now found a preferred method of preparing such catalysts having an improved crush strength as will be described below. The method is especially suitable when using a low acidity refractory binder. This method comprises the steps of:

(i) preparing an extrudable mass comprising a substantially homogenous mixture of metallosilicate crystallites, water, a source of the low acidity refractory oxide binder present as a mixture of a powder and a sol,
(ii) extruding the extrudable mass resulting from step (i),
(iii) drying the extrudate resulting from step (ii)and,
(iv) calcining the dried extrudate resulting from step (iii).

[0036] Catalyst particles obtained by the above process have an increased crushing strength. This is advantageous because such catalysts are typically applied in a packed bed reactor. Due to the normally high operating pressure and mass flows in the reactor strong catalyst particles are needed.

[0037] The description of the above method will further refer to a silica binder only. It will be understood that the below preferred conditions will, when applicable, also apply to other possible binders as here described.

[0038] Preferably the silica sol is an acid silica sol. The acid silica sol may be any colloidal silica having a pH lower than 7. When a pH value is mentioned the pH as measured in water of 18 °C is meant. An example of a suitable acid silica sol is Nyacol 2034DI (trademark of PQ Corp, Valley Forge, Pennsylvania) or Ultra-Sol 7H (trademark of RESI Inc, Newark). The silica powder may be commercially obtained silica powder, for example Sipernat 22 or 50 (trademark of Degussa AG), Nasilco Ultrasil VN3SP or HiSil 233 EP (trademark of PPG Industries). The solid silica powder particles preferably have a mean diameter of between 10 mm and 200 mm.

[0039] The surface of the acid silica sol particle comprises -OH groups. It is believed that for obtaining a catalyst particle having an even higher strength it is essential that during the mixing of the components in step (i)some or all of these groups are converted to O groups. This is preferably achieved by adding an amine compound in step (i). It has further been found that when adding an amine compound just before performing step (ii) an even more stronger catalyst particle is obtained. It is believed, although we do not wish to be bound to this theory, that the stronger catalyst is obtained because not all of the -OH groups on the sol particle surface are converted into -O- groups. Thus step (i) is preferably performed by first mixing the zeolite and the acid silica sol into a first homogeneous mixture and subsequently adding the amine compound to the first homogeneous mixture such that the pH of the resulting second mixture is raised from below 7 to a value of above 8. It can be easily determined by one skilled in the art, by straightforward experimentation, what the optimal moment in step (i) is for adding the amine compound. As a guideline it is preferred to add the amine compound during the second half of the time and more preferably in the last quarter of the time required to mix the components in step (i). Most preferably the amine compound is added within 20 minutes before performing step (ii).

[0040] Alternatively, a non-acid stabilized silica sol can also be used. The stabilization of the solmay be achieved by an alkaline or a non-ionic substance. Typical examples of this type of silica sols are commercially available in the Bindzil product range (Bindzil is a trademark of EKA Chemicals, Bohus, Sweden) in various compositions and intrinsic pH values.

[0041] Using such a non-acidic sol allows an alternative refinement of the extrusion recipe, where the order and timing of the addition of the component, such as the metallosilicate, the binder present in powder and sol form can be altered considerably without affecting dramatically the extrudability of the resulting mass. In these cases, the addition of the optional amine compound can even be performed at the beginning of the mixing.

[0042] The extrudable mass in step (i) should have a sufficient viscosity in order to be extruded into shapes. One skilled in the art will know how to achieve such a paste like mixture. For example by adding water in step (i) the viscosity can be lowered. The water content of the sol may be between 60 and 80 wt%. Preferably the water content of the extrudable mass as obtained in step (i) does not exceed 60%, and preferably is at least 35% by weight.

[0043] To obtain an even stronger catalysts it is preferred to maximise the amount of acid silica sol used relative the amount of silica powder used, while still achieving a sufficient viscosity of the extrudable mass. The optimal amount of silica powder to be used will depend on the zeolite content, wherein at a low zeolite content of the catalyst, more silica powder will have to be used. One skilled in the art can easily determine the optimal composition in view of the above teaching.

[0044] The amine compound is preferably a compound according to the general formula $R^1R^2R^3N$ in which R^1-R^3 may be hydrogen and/or an alkyl group having 1-6 carbon atoms. Examples are ammonia, methyl ethyl amine, triethyl amine, of which ammonia, is the most preferred. The amine compound should preferably be added in such an amount in order to raise the pH of the mass to alkaline conditions. Preferred conditions are a pH of the mixture obtained in step (i) of above 8. The pH will be lower than 14.

[0045] Step (i)may for example be performed at ambient conditions by first mixing the zeolite, optionally the silica powder and acid silica sol, subsequently adding an amine compound and optionally at the end of step (i) a plasticising agent. The plasticiser agent is used to increase the viscosity of the mixture in order to obtain an extrudable mass. Suitable plasticising agents are for example dextrose, gelatine, glucose, glues, gums, salts, waxes, starch and cellulose ethers. Some typical cellulose ether binders are methylcellulose, ethylhydroxy ethylcellulose, hydroxybutyl methylcellulose, hydroxymethylcellulose, hydroxypropyl methylcellulose,hydroxyethyl methylcellulose, hydroxybutylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, sodium carboxy methylcellulose, and mixtures thereof. Methylcellulose and/or methylcellulose derivatives are especially suited as organic binders in the practice of the present invention with methylcellulose, hydroxypropyl methylcellulose, or combinations of these being preferred. Preferred sources of cellulose ethers are Methocel A4M, F4M, F240, and K75M (Trademarks of Dow Chemical Co).

[0046] The extrusion in step (ii) may be performed by well known processes as for example illustrated in Perry's Chemical Engineers 'Handbook, McGRAW-HILL International Editions, sixth edition, 1984, p 8-60 to 8-66 and in Particle Size Enlargement, Handbook of powder Technology Vol. 1, Elsevier, 1980, p 112-121. Examples of such methods are extrusion performed by a screw extruder, a plate or ram extruder. The extrudates can have a wide variety of forms and sizes.

[0047] Drying step (iii) and calcining step (iv)may be performed under conditions well known to one skilled in the art. Step (iii), for example, may take place at a temperature of at least 60 °C to about 250 °C, for a time sufficient to dry the extrudate, for example, for at least 1 hour. Calcining step (iv), for example, may take place in air, or other inert gas, at temperatures ranging from 250 °C to 850 °C for periods of time ranging, for example, from about 1 to about 48 hours or more.

[0048] The product obtained in the catalytic dewaxing process according to the invention may optionally be subjected to a hydrofinishing step. Hydrofinishing is known in the art and examples of suitable hydrofinishing steps are disclosed in, for instance, US A 5139647, WO A 9201657 and WO-A-9201769. Generally, hydrofinishing comprises contacting a hydrocarbon feed, in this case a feed comprising the dewaxed lubricating base oil, with a hydrogenation catalyst under relatively mild conditions in order to saturate at least part of the aromatics still present in the dewaxed base oil. Suitable catalysts are those normally applied for this purpose with noble metal-based catalysts, such as those comprising Pt and/or Pd supported on an amorphous silica-alumina carrier or comprising Pt on an alumina support, being preferred options. Hydrofinishing conditions normally involve operating temperatures up to 350 °C and preferably between 150 and 300 °C, operating pressures from 10 to 200 bar and weight hourly space velocities of from 0.5 to 7.5 kg/1/h.

[0049] The effluent from the catalytic dewaxing process or optionally the effluent of a hydrofinishing treatment applied subsequently is separated into a gaseous fraction and a liquid fraction. Such separation or fractionation in steps (b) or (d) can be attained by conventional methods, such as by distillation under atmospheric or reduced pressure. Of these, distillation under reduced pressure, including vacuum flashing and vacuum distillation, is most suitably applied. The cutpoint(s) of the distillate fraction(s) is/are selected such that each product distillate recovered has the desired properties for its envisaged application. For lubricating base oils, the cutpoint will normally be at least 280 °C and will normally not exceed 550 °C, the exact cutpoint being determined by the desired product properties, such as volatility, viscosity, viscosity index and pour point. In a preferred embodiment, more than one base oil grades are prepared from hydrocarbon feed comprising a mixture of several refinery streams derived from naphthenic crude oils selected from coker gas oil, lube extracts, deasphalted oil, fuels distillates, and cracker residues, wherein the hydrocarbon feed comprises heteroatom species and aromatics and boils in the range of about 150°C to about 550°C (ASTM D2887).

[0050] The aniline point of a lubricating base oil is the temperature at which a mixture of aniline and oil separates, as determined according to ASTM D 611-01b. The aniline point provides a guidance on the solvability of the base oil with respect to materials which are in contact with the oil, such as additives and elastomers. The lower the aniline point the greater the solvency of the oil.

[0051] Preferably, a naphthenic base oil obtainable by the subject process has an aniline point of at most about 110 °C, as determined by American Standard Test Method (ASTM) D 611-01b, more preferably at most about 100 °C, more preferably at most about 95 °C, and even more preferably at most about 85 °C. Yet more preferably, a naphthenic base oil obtainable according to the process of the invention has an aniline point in the range of from 40°C to 100°C, preferably of from 45°C to about 85°C.

[0052] Preferably, a naphthenic base oil obtainable according to the process of the invention has a flash point of at least about 135°C (ASTM D92), more preferably of at least about 145°C.

[0053] Preferably, a naphthenic base oil obtainable according to the process of the invention has a viscosity index (VI) of less than 85, more preferably of less than 65; generally, VI value are obtained in the range of from 45 to 80 (as determined by ASTM D2270-04).

[0054] The invention will now be illustrated with the following non-limiting examples.

[0055] In the tables given in the working examples the following abbreviations are used: ppmw refers to parts per million on a weight basis; % wt refers to percent by weight, Vk40 and Vk100 refer to the kinematic viscosity at 40 °C and 100 °C, respectively, and are expressed in mm^2/s (centiStokes, cSt); VI stands for viscosity index and IBP and FBP refer to initial boiling point and final boiling point, respectively.

Example 1: Dewaxing of a DAO feed derived from a semi-naphthtenic crude oil with a dewaxing catalyst comprising a precious metal

[0056] A DAO (Deasphalted Oil) feed produced by a refinery from a semi-naphthenic crude oil was first contacted in the presence of hydrogen with a catalyst system containing two types of catalyst, i.e. a NiMo on alumina hydrotreating catalyst (LH-23, commercially available from Criterion Catalyst Company), and a NiW on amorphous silica-alumina hydrocracking catalyst (LH-21, commercially available from Criterion Catalyst Company). Table-1 shows the main characteristics of the feed.

[0057] The liquid product of this first process step was subsequently catalytically dewaxed in the presence of hydrogen with a 25% ZSM-12 / 75% silica impregnated with 0.7% wt Platinum dewaxing catalyst prepared according to Example 2b of EP-A- 1137741. The properties of the dewaxed products are given in Table-2 while the operating conditions for the hydrotreating and catalytic dewaxing step are given in Table-3

Table-1 DAO Feed properties

		DAO	method
VI		44	
Kinematic viscosity at 100°C		67.21	ASTM D 445
Color		8	ASTM 1500
Pour point	°C	+3	ASTM D 97
Nitrogen content	ppm wt	2019	ASTM D 5762

(continued)

		DAO	method
Sulphur content	%wt	0.132	ASTM D2622
460 °C+ content	%wt	81	ASTM D2887

Table-2 Product properties (>460 °C + fraction) after dewaxing

		DAO	method
VI		79	
Vk100)	mm^2/s	41.73	ASTM D 445-04
Pour point	°C	-9	ASTM D 97

Table-3 Process conditions

		DAO
Hydrotreating/cracking		
Total pressure	bar	150
Overall WHSV	T/m^3 h	0.4
Recycle gas rate	Nm^3/ton	1000
Temperature	°C	370
Catalytic Dewaxing (CDW)		
Total pressure	bar	150
WHSV	T/m^3 h	0.8
Recycle gas rate	Nm^3/ton	500
Temperature	°C	320
460°C + content in CDW Feed	%wt	64.2
460°C + content in CDW Product	%wt	63.3
460°C + dewaxing yield	%wt	98.6

[0058] The above tests were carried out with a precious metal dewaxing catalyst, but could also be carried out with similarly good results with a non precious metal dewaxing catalyst (SLD-800) in case that no very high saturates content (in excess of 98%wt) in the final product was desired. Further, similar results were obtained for employing dewaxing catalysts comprising either precious metal, or non-precious metal components with distillate fractions obtained from vacuum distillation of semi naphthenic crudes.

[0059] The above experiments show that naphthenic base oils can be obtained in high yields, and with good properties from semi-naphthenic or naphthenic crude oil feeds without significant yield loss due to cracking. Furthermore, the mild conditions employed make the process particularly interesting due to low energy requirements.

Claims

1. A process for producing at least one naphthenic base oil from a hydrocarbon feed containing heteroatom species and aromatics, comprising the steps of:

a) hydrotreating the feed under hydrotreating conditions effective for removing at least a portion of the heteroatom

species and saturating at least a portion of the aromatics to produce a first stage effluent having a reduced amount of heteroatom species; and
b) removing gaseous and liquid fractions boiling in the gas oil range from the effluent from step (a), and
c) dewaxing the effluent obtained in step (b) under catalytic dewaxing conditions in the presence of a catalyst composition comprising a molecular sieve containing covalently bound alumina moieties in its framework and having pores with a diameter in the range of from 0.35 to 0.80 nm, wherein the molecular sieve has been modified to reduce the mole percentage of alumina, to produce at least one effluent, and
d) fractionating the effluent obtained in step(c) to produce at least one naphthenic base oil grade.

2. The process according to claim 1 wherein the hydrocarbon feed is derived from a naphthenic API Group I crude oil.

3. Process according to claim 1 or claim 2, wherein the aluminosilicate zeolite crystallites is a MFI-type zeolite, a ferrierite group zeolite, a TON-type zeolite, an MTW-type zeolite or an MTT-type zeolite.

4. Process according to any one of claims 1-3, wherein the aluminosilicate zeolite crystallites have been subjected to a dealumination treatment.

5. Process according to claim 4, wherein the dealuminated aluminosilicate zeolite crystallites are obtained by contacting the aluminosilicate zeolite crystallites with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:

$$(A)_{2/b}SiF_6$$

wherein 'A' is a metallic or non-metallic cation other than H+ having the valence 'b', preferably ammonium.

6. Process according to any one of claims 3-5, wherein an extrudate of the aluminosilicate zeolite crystallites and the binder is contacted with the aqueous solution of the fluorosilicate salt.

7. Process according to any one of claims 1-6, wherein the hydrocarbon feed is a hydrotreated vacuum distillate fraction boiling between 300 and 620 °C (ASTM D2887), or a Deasphalted Oil (DAO).

8. Process according to any one of claims 1-7, wherein the hydrogenation component is palladium, platinum, nickel and or cobalt in sulphidic, oxidic and/or elemental form.

9. Process according to any one of claims 1-8, wherein the catalyst composition is obtained by performing at least the following steps:

(i) preparing an extrudable mass comprising a substantially homogenous mixture of metallosilicate crystallites, water, a source of the low acidity refractory oxide binder present as a mixture of a powder and a sol,
(ii) extruding the extrudable mass resulting from step (i),
(iii) drying the extrudate resulting from step (ii) and,
(iv) calcining the dried extrudate resulting from step (iii).

10. A naphthenic base oil obtainable according to the process according to any one of claims 1-9.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 10 9176

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 730 876 A (SEQUEIRA A) 1 May 1973 (1973-05-01) * column 2, line 38 - line 42 * * column 3, line 32 - line 37 * * column 4, line 35 - line 44 * * column 5, line 1 - line 11 * * claim 1; example 1 * -----	1-10	INV. C10G65/04 C10G65/08 C10G45/64
X	US 30 529 A (SUN OIL COMPANY) 24 February 1981 (1981-02-24) * column 1, line 33 - line 56 * * column 2, line 28 - line 44; claims 1,2,5; figure 1 * -----	1-10	
X	US 4 515 680 A (HETTINGER JR WILLIAM P [US] ET AL) 7 May 1985 (1985-05-07) * claims 1,6,7; figure 1 * -----	1-10	
X	WO 00/29511 A (SHELL INT RESEARCH [NL]; BALLEGOY CAROLUS MARIA VAN [NL]; CREYGHTON ED) 25 May 2000 (2000-05-25) * the whole document * -----	1-9	TECHNICAL FIELDS SEARCHED (IPC)
X	WO 2004/053027 A (SHELL INT RESEARCH [NL]; BENARD GERARD [FR]; DUPREY ERIC [FR]; MOUREAU) 24 June 2004 (2004-06-24) * the whole document * -----	1-9	C10G
X	WO 96/41849 A (SHELL INT RESEARCH [NL]; SHELL CANADA LTD [CA]) 27 December 1996 (1996-12-27) * the whole document * -----	1-9	
X	US 4 361 477 A (MILLER STEPHEN J) 30 November 1982 (1982-11-30) * column 3, line 33 - column 8, line 25; claims 1,2 * ----- -/--	1-9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	26 October 2007	Deurinck, Patricia

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 07 10 9176

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 3 663 430 A (MORRIS HERBERT C) 16 May 1972 (1972-05-16) * column 5, line 17 - line 29; claims 1-5,12; examples 6,7 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	26 October 2007	Deurinck, Patricia

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....
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 07 10 9176

26-10-2007

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3730876 A	01-05-1973	NONE	
US 30529 A		NONE	
US 4515680 A	07-05-1985	NONE	
WO 0029511 A	25-05-2000	AT 305499 T	15-10-2005
		AU 754266 B2	07-11-2002
		AU 1859400 A	05-06-2000
		CA 2350581 A1	25-05-2000
		CN 1330699 A	09-01-2002
		CN 1597860 A	23-03-2005
		DE 69927519 T2	14-06-2006
		DK 1137741 T3	13-02-2006
		ES 2251249 T3	16-04-2006
		HU 0104314 A2	28-03-2002
		JP 2002530470 T	17-09-2002
		RU 2235115 C2	27-08-2004
		US 6576120 B1	10-06-2003
WO 2004053027 A	24-06-2004	AU 2003300256 A1	30-06-2004
		BR 0317133 A	25-10-2005
		CA 2509369 A1	24-06-2004
		CN 1723263 A	18-01-2006
		JP 2006509090 T	16-03-2006
		KR 20050085488 A	29-08-2005
		MX PA05006160 A	26-08-2005
		US 2006065575 A1	30-03-2006
WO 9641849 A	27-12-1996	AT 188502 T	15-01-2000
		AU 755963 B2	02-01-2003
		AU 6303496 A	09-01-1997
		BR 9608802 A	17-02-1999
		CN 1193335 A	16-09-1998
		DE 69606035 D1	10-02-2000
		DE 69606035 T2	13-07-2000
		DK 832171 T3	08-05-2000
		ES 2142069 T3	01-04-2000
		JP 11507969 T	13-07-1999
		JP 3839848 B2	01-11-2006
		SK 169997 A3	05-08-1998
		US 5804058 A	08-09-1998
US 4361477 A	30-11-1982	NONE	
US 3663430 A	16-05-1972	NONE	

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4744884 A **[0007]**
- US 4699707 A **[0007]**
- US 5976354 A **[0008]**
- US 5336478 A **[0023]**
- EP 57049 A **[0023]**
- EP 65400 A **[0023]**
- US 3832449 A **[0023]**
- EP 513118 A **[0023]**
- EP 59059 A **[0023]**
- EP 162719 A **[0023]**
- US 4076842 A **[0023]**
- US 4619820 A **[0023]**
- EP 522196 A **[0023]**
- EP 108486 A **[0023]**
- EP 42226 A **[0023]**
- US 4016218 A **[0024]**
- WO 9641849 A **[0030]**
- US 5157191 A **[0030]**
- US 5139647 A **[0048]**
- WO 9201657 A **[0048]**
- WO 9201769 A **[0048]**
- EP 1137741 A **[0057]**

Non-patent literature cited in the description

- *Ind. Eng. Chem. Res.,* 1991, vol. 30, 12-18 **[0032]**
- Perry's Chemical Engineers 'Handbook. McGRAW-HILL International Editions, 1984, 8-608-66 **[0046]**
- Handbook of powder Technology. Particle Size Enlargement. Elsevier, 1980, vol. 1, 112-121 **[0046]**