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(57) **ABSTRACT**

Process to prepare base oils from a Fischer-Tropsch synthesis product by (a) separating the Fischer-Tropsch synthesis product into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii), (b) subjecting the base oil precursor fraction (ii) to a catalytic hydroisomerisation step in the presence of a catalyst comprising a binder, zeolite Beta and a Group VIII metal and a catalytic dewaxing step in the presence of a catalyst comprising a binder, a medium pore size zeolite having and a Group VIII hydrogenation component to yield one or more base oil grades, (c) subjecting the heavy ends fraction (iii) to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii) and (d) subjecting the high boiling fraction (v) of fraction (iv) to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades.

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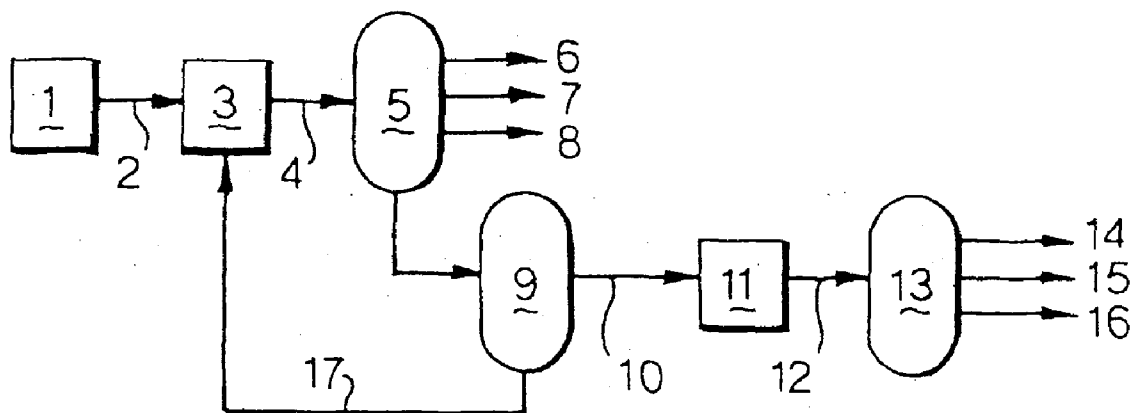


Fig.1.

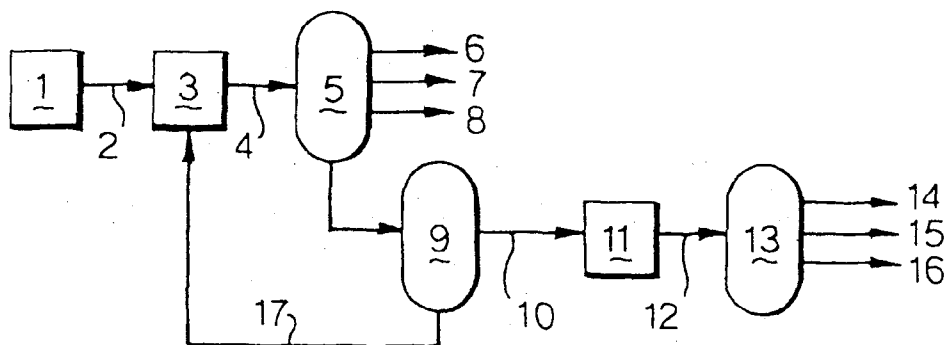


Fig.2.

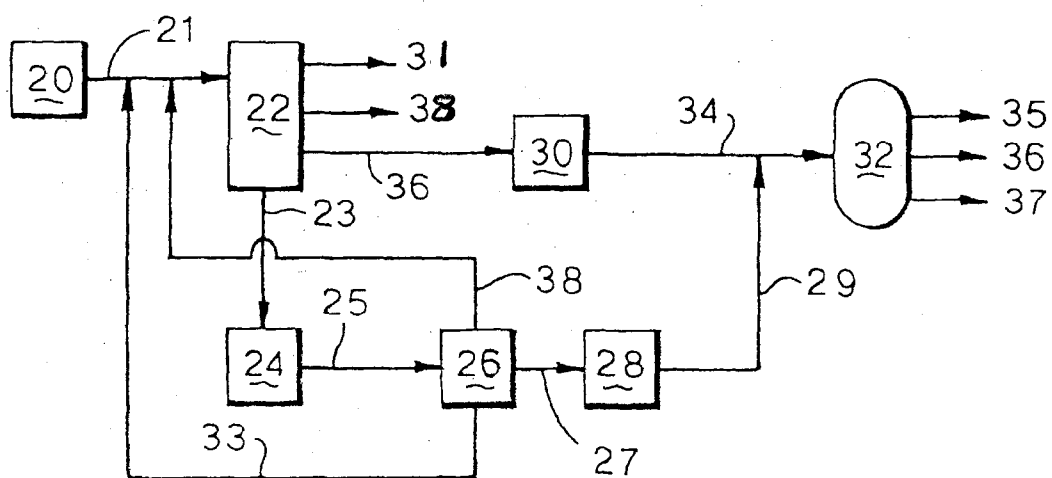
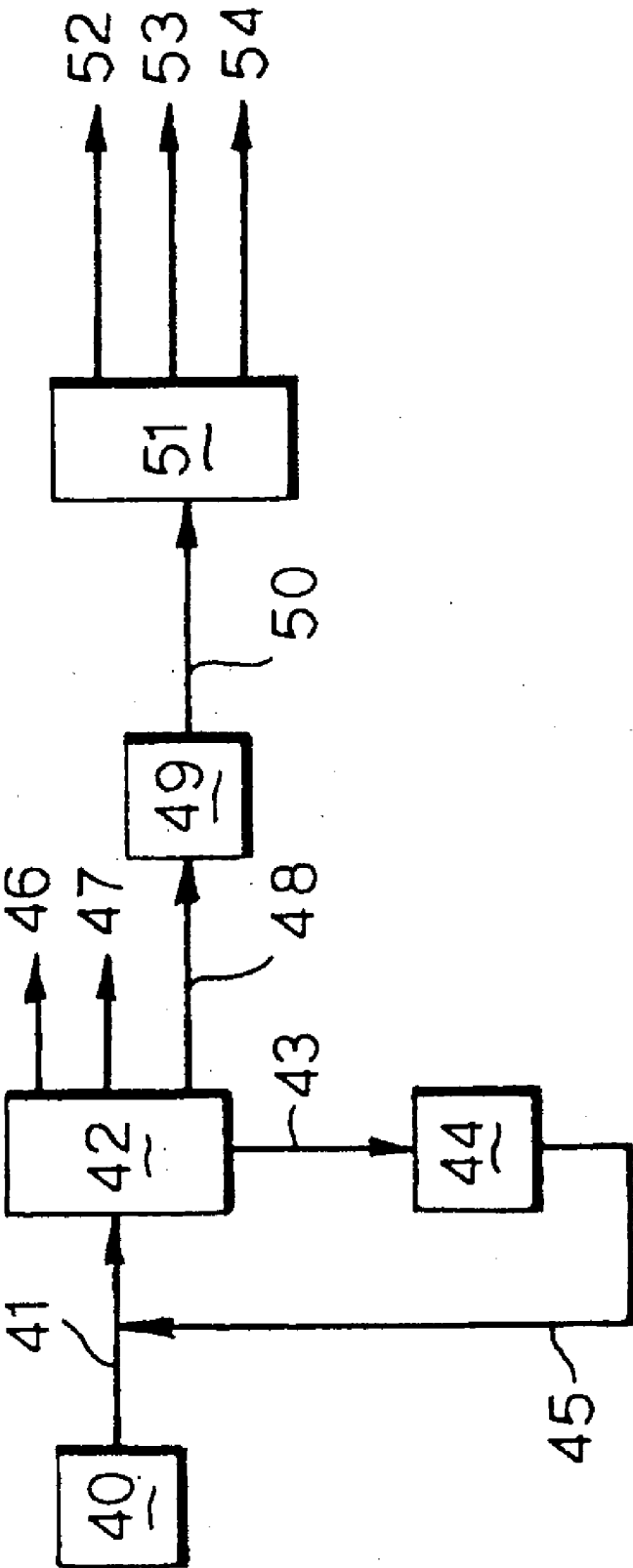


Fig.3.



PROCESS TO PREPARE A BASE OIL FROM A FISCHER-TROPSCH SYNTHESIS PRODUCT

[0001] The present invention is directed to a process to prepare base oils or the intermediate waxy raffinate product in a high yield from a Fischer-Tropsch synthesis product.

[0002] Such processes are known from WO-A-9941332, U.S. Pat. No. 6,080,301, EP-A-0668342, U.S. Pat. No. 6,179,994, U.S.-A-2004/0065581 or WO-A-02070629. These processes all comprise some kind of hydroisomerisation of the Fischer-Tropsch synthesis product followed by a dewaxing step of the higher boiling fraction obtained in said hydroisomerisation.

[0003] WO-A-02070629, for example, describes a process wherein the C5 plus fraction of a Fischer-Tropsch synthesis product is first subjected to a hydrocracking/hydroisomerising step in the presence of a catalyst consisting of platinum on an amorphous silica-alumina carrier. The effluent of this conversion step is separated into middle distillate products and a base oil precursor fraction and a higher boiling fraction. The base oil precursor fraction is catalytically dewaxed in the presence of a platinum-ZSM-5 based catalyst and the heavy fraction is recycled to the hydrocracking/hydroisomerising step.

[0004] Although such a process will yield excellent quality base oils there is room for improvement. Especially the yield of base oils relative to the Fischer-Tropsch synthesis product may be improved. More especially for base oils having a kinematic viscosity at 100° C. of between 2 and 8 cSt an improved yield would be welcome.

[0005] EP-A-776959 discloses a process to prepare base oil in a high yield from a narrow boiling Fischer-Tropsch wax by first performing a hydroisomerisation step in the presence of an amorphous catalyst system followed by a catalytic dewaxing step using a platinum/ZSM-23 catalyst.

[0006] U.S.-A-2004/0065581 also discloses the preparation of a base oil in a high yield from a narrow cut Paraffint C80 wax, which is a substantially normal paraffin wax having a melting point of about 80° C., by contacting the feed with a stack of platinum/zeolite Beta and platinum/ZSM-48.

[0007] The above two processes describe a high yield to base oils relative to the narrow cut feed. If calculated on the entire Fischer-Tropsch wax, which may boil well above the boiling range of the feeds disclosed in these publications, the yield will be much lower.

[0008] The present invention aims at providing a process, which will make more base oils relative to the entire Fischer-Tropsch synthesis product as boiling in the base oil range and above.

[0009] The following process achieves this object. Process to prepare base oils from a Fischer-Tropsch synthesis product by

[0010] (a) separating the Fischer-Tropsch synthesis product into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii),

[0011] (b) subjecting the base oil precursor fraction (ii) to a catalytic hydroisomerisation step in the presence of a catalyst comprising a binder, zeolite Beta and a Group VIII metal and a catalytic dewaxing step in the presence of a catalyst comprising a binder, a medium pore size zeolite

having and a Group VIII hydrogenation component to yield one or more base oil grades,

[0012] (c) subjecting the heavy ends fraction (iii) to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii) and

[0013] (d) subjecting the high boiling fraction (v) of fraction (iv) to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades.

[0014] Applicants have found that by directly subjecting the fraction of the intermediate fraction (ii) of the Fischer-Tropsch synthesis product and the high boiling fraction (v) as obtained in step (c) to a selective isomerisation and dewaxing step a higher yield to base oils relative to the Fischer-Tropsch synthesis product can be obtained.

[0015] Without intending to be bound by the following theory it is believed that the high yield to base oils is achieved in that the present process yields more of the fraction boiling in the base oil range, i.e. fractions (ii) and (v), as suitable feed to the catalytic hydroisomerisation and catalytic dewaxing processes of steps (b) and (d). In the prior art process of WO-A-02070629 the boiling in the base oil range of the Fischer-Tropsch synthesis product was first contacted with a catalyst which would convert a large part to middle distillate products and lower boiling products. By using this different line-up the conversion of potential base oil molecules in the Fischer-Tropsch synthesis product to middle distillate molecules is minimized. Furthermore in the process of WO-A-02070629 the heavy fraction as obtained in the hydrocracking/hydroisomerising step is recycled to said step. This results in that more potential base oil molecules are converted to middle distillate molecules.

[0016] The Fischer-Tropsch synthesis product can be obtained by well-known processes, for example the so-called Sasol process, the Shell Middle Distillate Synthesis Process or by the ExxonMobil "AGC-21" process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, U.S. Pat. No. 4,943,672, U.S. Pat. No. 5,059,299, WO-A-9934917 and WO-A-9920720. Typically these Fischer-Tropsch synthesis products will comprise hydrocarbons having 1 to 100 and even more than 100 carbon atoms. The hydrocarbon product will comprise iso-paraffins, n-paraffins, oxygenated products and unsaturated products. The feed to step (a) or any fractions obtained in step (a) may be hydrogenated in order to remove any oxygenates or unsaturated products. The process of the present invention is especially advantageous when a substantial part, preferably more than 10 wt %, more preferably more than 30 wt % and even more preferably more than 50 wt % of the Fischer-Tropsch synthesis product boils above 550° C. An example of a suitable process which may prepare such a heavy Fischer-Tropsch synthesis product is described in WO-A-9934917.

[0017] In step (a) the Fischer-Tropsch synthesis product is separated into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) preferably, having an initial boiling point between 500 and 600° C. and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii). Preferred base oil precursor fractions (ii) comprise for more than 90 wt % of compounds boiling between 370 and 600° C. Suitably the Fischer-Tropsch synthesis product is first fractionated at atmospheric pressure or higher to obtain fraction (i) boiling in the middle distillate range and below. Fractionation may be performed by flashing or distillation. The middle distillate range is sometimes defined as the fraction boiling predominately, i.e. for

more than 90 wt %, between 200 and 350° C. and it comprises the gas oil and kerosene fractions, which can be isolated from the Fischer-Tropsch synthesis product. The residue or bottom product of the atmospheric fractionation is further separated at near vacuum pressure to the heavy ends fraction (iii) having an initial boiling point between 500 and 600° C. and the intermediate base oil precursor fraction (ii). More preferably the T10 wt % recovery point of the heavy ends fraction (iii) is between 500 and 600° C.

[0018] In step (b) the base oil precursor fraction (ii) is first passed over a catalyst comprising a binder, zeolite Beta and a Group VIII metal. The resulting intermediate product is then further subjected to a catalytic dewaxing step. These first and second stages can be operated as separated steps. Preferably both stages are integrated process steps, for example cascaded. Zeolite Beta catalysts are 12 ring acidic silica/alumina zeolites with or without boron, wherein boron replaces some of the aluminum atoms. Pre-sulfided Zeolite Beta is preferred when some residual sulfur in the product is acceptable and when the base oil precursor fraction contains some sulphur. In cases wherein part of the base oil precursor fraction (ii) is prepared in step (c) using a sulphided catalyst a sulphur containing base oil precursor fraction may be suitably prepared as feed to step (b) in one of the preferred embodiments of the present invention as illustrated in FIG. 3 wherein steps (b) and (d) are combined.

[0019] Zeolite Beta as used in the first stage catalyst preferably has an Alpha value below 15, more preferably below 10, at least prior to metal loading. Alpha is an acidity metric that is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst. Alpha is a relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). Alpha is based on the activity of the highly active silica-alumina cracking catalyst taken as an Alpha of 1 as described in U.S. Pat. No. 3,354,078 and measured at 538° C. as described in the Journal of Catalysis, vol. 4, p. 527 (1965); vol. 6, p. 278 (1966); and vol. 61, p. 395 (1980). The use of Fischer Tropsch derived base oil precursor fraction requires a low Alpha value of the Zeolite Beta catalyst due to minimal nitrogen content in the feeds. Alpha values may be reduced by steaming. Examples of suitable first stage catalysts are described in the earlier referred to U.S.-A-2004/0065581.

[0020] The catalyst of the second stage in of step (b) comprises a medium pore size molecular sieve. Preferably the intermediate pore size molecular sieves are zeolites having a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48 or combinations of said zeolites. Most preferred are ZSM-48, SSZ-32, ZSM-23, ZSM-12 and ZSM-22, of which ZSM-48 is very suitable. Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in U.S. Pat. No. 4,859,311.

[0021] The first stage or second stage catalyst of step (b) suitably comprises 0.01-5 wt % of at least one Group VIII metal (i.e., Fe, Ru, Os, Co, Rh, Ir, Pd, Pt, Ni). Platinum and palladium are most preferred. Platinum or palladium blended with each other or other group VIII metals follow in preference. Nickel may also be blended with group VIII precious metals and is included in the scope of the invention whenever group VIII blends, alloys, or mixtures are mentioned. Pre-

ferred metal loading on both catalysts are 0.1-1 wt % with approximately 0.6 wt % most preferred.

[0022] The binder of the first stage or second stage catalyst of step (b) 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. A suitable binder is alumina. If alumina is used the content of the binder in the catalyst is preferably between 10 and 65 wt %. More preferably a low acidity refractory oxide binder material, which is essentially free of alumina, is used. Examples of these binder materials are 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. If a low acidity binder is used the content of the binder is preferably between 60 and 95 wt %, more preferably between 65 and 90 wt %.

[0023] Catalysts comprising the low acidity binder as described above are preferably subjected to a dealumination treatment. In such a treatment the surface of the aluminosilicate zeolite crystallites will be modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example U.S. Pat. No. 5,157,191 or WO-A-2000029511. Examples of suitable dewaxing catalysts as described above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated Pt/ZSM-22, as for example described in WO-A-200029511 and EP-B-832171.

[0024] The crystallite size of the medium pore size zeolite and/or the zeolite beta may be as high as 100 micron. 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 0.1 micron. 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. Preferable catalysts are used having a crystallite size of between 0.05 and 0.2 µm and which have been subjected to a dealumination treatment. The size or better said the length of the crystallite in the direction of the pores is the critical dimension. X-ray diffraction (XRD) can be used to measure the crystallite length by line broadening measurements.

[0025] The process conditions in both first and second stage include a hydrogen pressures in the range of from 10 to 200 bar, preferably from 40 to 70 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.

[0026] The first stage reaction step of step (b) involving the Beta catalyst is preferably performed at temperatures

between 200 and 370° C., more preferably at between 260 and 340° C. and most preferably at 270 and 300° C.

[0027] The second stage reaction step of step (b) is preferably performed at temperatures between 260 and 430° C., more preferably at between 320 and 370° C. and most preferably at 330 and 350° C. The temperature at which the two stages of step (b) are performed are preferably controlled independently. The pressure in both stages is preferably similar to each other. In a preferred embodiment of the invention, a cascaded two-bed catalyst system consisting of a first bed Pt/Beta catalyst followed by a second bed of a catalyst comprising platinum and one of the medium pore size zeolites mentioned above allows a highly selective process for preparing base oils from the base oil precursor fraction (ii) with minimal gas formation. In cascading, the intermediate product preferably directly passes from the first bed to the second bed without inter-stage separation. Optionally, light byproducts (e.g., methane, ethane) can be removed between the first and second stage.

[0028] The base oil precursor fraction to step (b) may be the fraction of the Fischer-Tropsch wax as synthesized. Such a fraction will usually comprise for more than 95 wt % of normal paraffins. Preferably the feed to step (b) also comprises fraction (v) as obtained in step (c). This fraction (v) will comprise for a substantial portion of iso-paraffins. The presence of iso-paraffins is advantageous because these molecules require less isomerisation as compared to the normal paraffins for achieving the desired pour point of the base oil. The lower congealing point of this combined base oil precursor fraction is indicative for the presence of iso-paraffins. The congealing point is therefore preferably lower than 80° C., more preferably lower than 60° C. and even more preferably lower than 50° C. The lower limit will typically be above 0° C. After performing a dewaxing step (b) the desired base oil(s) are preferably isolated from the dewaxed effluent in a base oil recovery step (e). In this step (e) lower boiling compounds formed during catalytic dewaxing are removed, preferably by means of distillation, optionally in combination with an initial flashing step. By choosing a suitable narrow distillation cut as feed to step (b) in step (a) it is possible to obtain a desired base oil directly after a catalytic dewaxing step (b) without having to remove any higher boiling compounds from the effluent of step (b). Preferred narrow cut feeds have a difference between its 90 % wt boiling point and its 10 % wt boiling point ($T_{90}-T_{10}$) in the range of from 40 to 150° C., more preferably from 50 to 130° C. Examples of very suitable grades are base oils having a kinematic viscosity at 100° C. of between 3.5 and 6 cSt.

[0029] It has also been found possible to make more than one viscosity grade base oil with the process according to the invention. By obtaining a base oil precursor fraction (ii) in step (a) having a more broad boiling range more base oil grades may advantageously be obtained in step (e). Preferably the difference between the T10 wt % recovery point and the 90 wt % recovery point in the boiling curve is larger than 100° C., more preferably larger than 150° C. In this mode the effluent of step (b) is separated into various distillate fractions comprising two or more base oil grades. In order to meet the desired viscosity grades and volatility requirements of the various base oil grades preferably off-spec fractions boiling between, above and/or below the desired base oil grades are also obtained as separate fractions. These fractions and any fractions boiling in the gas oil range or below may advantageously be recycled to step (a). Alternatively fractions

obtained boiling in the gas oil range or below may suitably be used as a separate blending component to prepare a gas oil fuel composition.

[0030] The separation into the various fractions in step (e) may suitably be performed in a vacuum distillation column provided with side strippers to separate the fraction from said column. In this mode it is found possible to obtain for example a 2-3 cSt product, a 4-6 cSt product and a 7-10 cSt product simultaneously from a single broad boiling base oil precursor fraction (ii). The viscosity values are the kinematic viscosity at 100° C.

[0031] In step (c) the heavy ends fraction (iii) is subjected to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii). Step (c) may be performed by any conversion process capable of converting the heavy Fischer-Tropsch wax to lower boiling hydrocarbon compounds. If the conversion product of step (c) is to contain a high content of olefinic compounds preferably a conversion process is applied which operates in the absence of added hydrogen. Examples of suitable processes which operate in the absence of added hydrogen are the well known thermal cracking process as for example described in U.S. Pat. No. 6,703,535 and the catalytic cracking process as for example described in U.S. Pat. No. 4,684,759. If on the other hand the conversion product of step (c) is to contain almost no olefins preferably a process is applied which is performed in the presence of added hydrogen. An example of a suitable process is the well known hydroisomerisation/hydrocracking process. Preferably the latter type of conversion process is preferred in the process according to the present invention in order to minimise the olefins content in the final base oil products.

[0032] The hydroconversion/hydroisomerisation reaction of step (c) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction of which some will be described in more detail below. The catalyst may in principle be any catalyst known in the art to be suitable for isomerising paraffinic molecules. In general, suitable hydroconversion/hydroisomerisation catalysts are those comprising a hydrogenation component supported on a refractory oxide carrier, such as amorphous silica-alumina (ASA), alumina, fluorided alumina, molecular sieves (zeolites) or mixtures of two or more of these. One type of preferred catalysts to be applied in the hydroconversion/hydroisomerisation step in accordance with the present invention are hydroconversion/ hydroisomerisation catalysts comprising platinum and/or palladium as the hydrogenation component. A very much preferred hydroconversion/hydroisomerisation catalyst comprises platinum and palladium supported on an amorphous silica-alumina (ASA) carrier. The platinum and/or palladium is suitably present in an amount of from 0.1 to 5.0% by weight, more suitably from 0.2 to 2.0% by weight, calculated as element and based on total weight of carrier. If both 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. Examples of suitable noble metal on ASA catalysts are, for instance, disclosed in WO-A-9410264 and EP-A-0582347. Other suitable noble metal-based catalysts, such as platinum on a fluorided alumina carrier, are disclosed in e.g. U.S. Pat. No. 5,059,299 and WO-A-9220759.

[0033] A second type of suitable hydroconversion/hydroisomerisation catalysts are those comprising at least one Group VIB metal, preferably tungsten and/or molybdenum,

and at least one non-noble Group VIII metal, preferably nickel and/or cobalt, as the hydrogenation component. Both metals may be present as oxides, sulphides or a combination thereof. The Group VIB metal 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 the carrier. The non-noble Group VIII metal is suitably present in an amount of from 1 to 25 wt %, preferably 2 to 15 wt %, calculated as element and based on total weight of carrier. A hydroconversion catalyst of this type which has been found particularly suitable is a catalyst comprising nickel and tungsten supported on fluorided alumina.

[0034] The above non-noble metal-based catalysts are preferably used in their sulphided form. In order to maintain the sulphided form of the catalyst during use some sulphur needs to be present in the feed. Preferably at least 10 ppm and more preferably between 50 and 150 ppm of sulphur is present in the feed. A possible source of sulphur are for example vacuum distillate or atmospheric residues of crude petroleum sources. Preferred sources are gas field condensates. These sources may be co-fed to step (c) in order to achieve the desired level of sulphur.

[0035] A preferred catalyst, which can be used in a non-sulphided form, comprises a non-noble Group VIII metal, e.g., iron, nickel, in conjunction with a Group IB metal, e.g., copper, supported on an acidic support. Copper is preferably present to suppress hydrogenolysis of paraffins to methane. The catalyst has a pore volume preferably in the range of 0.35 to 1.10 ml/g as determined by water absorption, a surface area of preferably between 200-500 m²/g as determined by BET nitrogen adsorption, and a bulk density of between 0.4-1.0 g/ml. The catalyst support is preferably made of an amorphous silica-alumina wherein the alumina may be present within wide range of between 5 and 96 wt %, preferably between 20 and 85 wt %. The silica content as SiO₂ is preferably between 15 and 80 wt %. Also, the support may contain small amounts, e.g., 20-30 wt %, of a binder, e.g., alumina, silica, Group IVA metal oxides, and various types of clays, magnesia, etc., preferably alumina or silica.

[0036] The preparation of amorphous silica-alumina microspheres has been described in Ryland, Lloyd B., Tamele, M. W., and Wilson, J. N., *Cracking Catalysts, Catalysis: volume VII*, Ed. Paul H. Emmett, Reinhold Publishing Corporation, New York, 1960, pp. 5-9.

[0037] The catalyst is prepared by co-impregnating the metals from solutions onto the support, drying at 100-150° C., and calcining in air at 200-550° C. The Group VIII metal is present in amounts of about 15 wt % or less, preferably 1-12 wt %, while the Group IB metal is usually present in lesser amounts, e.g., 1:2 to about 1:20 weight ratio respecting the Group VIII metal.

[0038] A typical catalyst is shown below:

Ni, wt %	2.5-3.5
Cu, wt %	0.25-0.35
Al ₂ O ₃ —SiO ₂ wt %	65-75
Al ₂ O ₃ (binder) wt %	25-30
Surface Area	290-325 m ² /g
Pore Volume (Hg)	0.35-0.45 ml/g
Bulk Density.	

[0039] The hydroconversion/hydroisomerisation conditions involve a feed that is contacted with hydrogen in the

presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380° C., preferably higher than 250° C. and more preferably from 300 to 370° C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 NI/l/hr, preferably from 500 to 5000 NI/l/hr. The hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 NI/kg and is preferably from 250 to 2500 NI/kg.

[0040] The conversion in step (c) as defined as the weight percentage of the feed boiling above 370° C. which reacts per pass to a fraction boiling below 370° C. is preferably at least 20 wt %, more preferably at least 25 wt %, preferably not more than 80 wt %, more preferably not more than 70 wt % and even more preferably not more than 65 wt %.

[0041] Preferably the effluent of the above combined steps (c) and (d) is provided to the same above described base oil work up section (step (e)). This is advantageous because the isolation of all base oil grades, including the heavier grade, may then be performed in the same distillation column(s).

[0042] In step (d) the high boiling fraction (v) of fraction (iv) is subjected to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades. The high boiling fraction (v) in the effluent of step (c) preferably has a initial boiling point of between 340 and 400° C. More preferably the 10 wt % recovery point is between 340 and 400° C. Preferably the fraction (v) comprises for more than 90 wt % of compounds boiling between 370 and 600° C. The final boiling point of said fraction (v) is preferably between 500 and 600° C. More preferably the 90 wt % recovery point is between 500 and 600° C. The catalytic dewaxing of step (d) may be performed using the first or second stage dewaxing processes as described above for step (b). These processes may be used alone or more preferably in the combination as described for step (b). Separations are preferably performed by means of distillation. Preferably the base oils are isolated from the effluent of step (d) in the same base oil work-up section (step (e)) as described above.

[0043] The fraction of the effluent of step (c) which boils above fraction (v), i.e. the so-called unconverted part of the feed to step (c), may be suitably recycled to step (c). Because the wax content of this fraction is lower than the wax fraction of the feed to step (c) it has been found possible to prepare a high viscous base oil from said fraction. This can be done by means of catalytic dewaxing, solvent dewaxing or combinations of said processes. A suitable combined process includes a first reduction of the wax content to between 5 and 40, preferably 5 and 30 wt % by means of catalytic dewaxing, and a subsequent solvent dewaxing step of the resultant product to obtain a haze free base oil. Catalytic dewaxing may be performed by means of well known dewaxing technology or by the first and second stage dewaxing processes as described for step (b). Applicants have found that a platinum/ZSM-12 catalyst is suitable for reducing the wax content while maintaining a high yield to the more viscous base oils. The kinematic viscosity at 100° C. of these haze free base oils is preferably above 10 cSt, more preferably above 14 cSt and may range to values of 30 cSt and above.

[0044] Preferably step (b) and (d) are combined. In such an embodiment it is preferred to provide the effluent of step (c) to step (a). This is advantageous because it reduces the number of distillation columns. In step (a) a mixture of fresh Fischer-Tropsch synthesis product and step (c) effluent will be separated simultaneously into again a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii). In this embodiment step (b) and (d) are performed in the same reactor, which is also advantageous for obvious reasons.

[0045] The Fischer-Tropsch synthesis product may contain olefins and oxygenates which may be detrimental for the hydroconversion catalysts used in step (b), (c) and (d). These compounds may be removed by means of hydrogenation of the Fischer-Tropsch synthesis product prior to performing step (a) or hydrogenation of the feeds to the separate steps (b), (c) and/or (d). The latter is advantageous because some of the oxygenates and/or olefins present in the Fischer-Tropsch synthesis product will end up in the middle distillate fraction (i) and could serve as lubricity enhancers in the resulting gas oil or kerosene fractions. The advantages of the presence of such compounds are for example described in EP-A-885275.

[0046] Possible hydrogenation processes are for example described in EP-B-668342. The mildness of the hydrotreating step is preferably expressed in that the degree of conversion in this step is less than 20 wt % and more preferably less than 10 wt %. The conversion is here defined as the weight percentage of the feed boiling above 370° C., which reacts to a fraction boiling below 370° C. Examples of possible hydrogenation processes involve the use of nickel containing catalysts, for example nickel on alumina, nickel on silica-alumina nickel on Kieselguhr, copper nickel on alumina, cobalt on silica-alumina or platinum nickel on alumina. The hydrogenation conditions are typical conditions for these type of processes, well known to the skilled person.

[0047] The invention will also be illustrated by making use of FIGS. 1-3.

[0048] FIG. 1 illustrates a state of the art process of WO-A-02070629.

[0049] FIG. 2 illustrates a process according to the invention.

[0050] FIG. 3 illustrates a process according to the invention.

[0051]

[0052] FIG. 1 describes a state of the art process line-up according to WO-A-02070629 illustrating a Fischer-Tropsch synthesis process step 1 wherein a Fischer-Tropsch product 2 is prepared. This product 2 is fed to a hydrocracking/hydroisomerisation step 3. Product 4 is subsequently separated in an atmospheric distillation column 5 into a naphtha product 6, a kerosene product 7, a gas oil product 8 and a bottoms product. The bottoms product is subsequently separated in a vacuum distillation column 9 into a base oil precursor fraction 10 and a higher boiling fraction 17. The fraction 10 is subsequently catalytically dewaxed 11 and the dewaxed oil 12 is fractionated in column 13 into various base oil products 14, 15 and 16. The higher boiling fraction 17 is recycled to hydrocracking/hydroisomerisation step 3.

[0053] FIG. 2 illustrates an embodiment of the present invention. In a Fischer-Tropsch synthesis process step 20 a Fischer-Tropsch product 21 is prepared. This product 21 is separated by means of distillation 22 in one or more middle distillate fractions 31, 38, which may be naphtha, kerosene

and gas oil, into a base oil precursor fraction 36 and a higher boiling fraction 23. Distillation 22 may be a atmospheric distillation and a vacuum distillation scheme as in FIG. 1. The base oil precursor fraction is fed to a catalytic hydroisomerisation step and a catalytic dewaxing step as combined in 30 to perform step (b) and the dewaxed oil 34 is fractionated in column 32 into one or more base oil products 35, 36 and 37. The higher boiling fraction 23 is fed to a hydrocracking/hydroisomerisation step 24 yielding a cracked product 25. From this product 25 a fraction boiling in the gas oil range and below 38, a base oil precursor fraction 27 and a higher boiling fraction 33 is separated in column 26. The base oil precursor fraction 27 is catalytically dewaxed 28 and the dewaxed oil is combined with dewaxed oil 34 to be separated in 32 as described above wherein base oil 37 is more viscous than base oil 16 of FIG. 1.

[0054] FIG. 3 is a process as in FIG. 2 wherein the products obtained in the hydrocracking/hydroisomerisation step 44 is recycled to the first separation unit 42. As can be seen by comparing FIG. 2 with FIG. 3 a considerable reduction in unit operations is achieved. In a Fischer-Tropsch synthesis process step 40 a Fischer-Tropsch product 41 is prepared. This product 41 is separated by means of distillation 42 in one or more middle distillate fractions 46, 47, which may be naphtha, kerosene and gas oil, into a base oil precursor fraction 48 and a higher boiling fraction 43. Distillation 42 may be an atmospheric distillation and a vacuum distillation scheme as in FIG. 1. The higher boiling fraction 43 is fed to a hydrocracking/hydroisomerisation step 44 yielding a cracked product 45, which is recycled to distillation 42.

[0055] The base oil precursor fraction 48 is fed to a catalytic hydroisomerisation step and a catalytic dewaxing step as combined in 49 and the dewaxed oil 50 is fractionated in column 51 into one or more base oil products 53 and 54. Base oil 54 will have a comparable viscosity as base oil 16 of FIG. 1.

[0056] The gas oil product 52 as separated from the dewaxed oil is preferably blended with the gas oil fraction 47 such to obtain a blended product having favorable low temperature properties. The gas oil product 52 will have a low cloud point and cold filter plugging point (CFFP). The volume of the gas oil product 52 having the favorable low temperature properties may be controlled by adjusting the initial boiling point of the base oil precursor fraction 48. Such a control allows the operator to target the low volume of gas oil 52 and thus also the temperature properties, such as cloud point and CFFP of the resulting blend of gas oil products 52 and 47.

[0057] The invention will be illustrated by the following non-limiting examples.

EXAMPLE 1

[0058] A Fischer-Tropsch derived product having the properties as listed in Table 1 was distilled into fraction boiling substantially above 540° C. (recovered 72 wt % on feed to distillation) and a fraction boiling substantially between 350 and 540° C. (recovered as 25 wt % on feed to distillation). In addition 3 wt % of a fraction boiling substantially below 350° C. was separated from the feed. The boiling curve data of the feed and the main distillate fractions are listed in Table 1.

TABLE 1

Sample	Fischer-Tropsch derived product (feed) (% weight fraction boiling below listed boiling point) (% weight)	350° C.-540° C. fraction (% weight)	540° C.+ fraction
320° C.	5.5	5.8	1.6
350° C.	7.6	13.0	1.6
370° C.	9.3	22.2	1.6
400° C.	12.2	34.4	1.6
450° C.	17.4	64.3	1.6
500° C.	23.9	91.1	2.2
540° C.	29.5	99.0	6.6
590° C.	35.9		16.6
700° C.	51.6		43.6

[0059] The 540° C.+fraction of Table 1 was subjected to a hydrocracking step wherein the feed was contacted with a 0.8 wt % platinum on amorphous silica-alumina carrier. The conditions in the hydrocracking step were: a fresh feed Weight Hourly Space Velocity (WHSV) of 0.9 kg/l.h, no recycle, and hydrogen gas rate=1100 NL/kg feed, total pressure=32 bar. The reactor temperature was varied as listed in Table 2. The hydrocracker effluent was analysed and the yields for the different boiling fractions are listed in Table 2.

TABLE 2

	Example			
	1-a	1-b	1-c	1-d
Reactor Temperature, ° C.	349	344	353	358
Fraction boiling below 370° C. (wt %)	69.8	47.1	82.2	95.1
Fraction boiling between 370 and 540° C. (wt %)	17.8	19.4	11.0	3.6

[0060] Thus relative to the feed to the distillation step 25 wt % of a fraction (I) boiling between 350 and 540° C. comprising substantially of n-paraffins is obtained in the distillation step and 14 wt % of a waxy raffinate fraction (II) boiling between 370 and 540° C. is obtained in the hydrocracking step. These two fractions (I) and (II) may be combined and a base oil may be prepared from this combined fraction by dewaxing.

[0061] To calculate the potential base oil yield on these fractions (i) and (ii) we base ourselves on the reported base oil yields as shown in FIG. 1 of U.S.-A-2004/0065581. The base oil yield for a base oil having a pour point of -20° C. is 60 wt % in a process wherein a substantially normal paraffin C24-C60 wax was dewaxed over a platinum/zeolite beta and platinum/ZSM-48 stacked catalyst system. It should be borne in mind that these yields are based on a substantially normal paraffin feedstock while in the present invention a partly isomerised feedstock will be dewaxed. Thus the 60 wt % yield on feed will provide a conservative overall yield for Example 1.

[0062] Thus 60 wt % of the combined fraction (I) and (II) will yield a base oil. Thus the total yield of base oil calculated on feed is 0.6*(25 wt % + 14 wt %)=23.4 wt %.

COMPARATIVE EXPERIMENT A

[0063] Example 1 was repeated except that the Fischer-Tropsch derived product (feed) was directly submitted to the hydrocracker step. No prior distillation was performed. The yield to the 370-540° C. fraction on feed was 24 wt %. Because this fraction is also partly hydroisomerised the same estimated base oil yield as for example 1 may be applied. The base oil yield will then be (0.6*24 wt %)=14.4 wt % on feed.

[0064] As can be seen by comparing Example 1 and comparative experiment A is that the base oil yield on Fischer-Tropsch derived product (feed) is significantly higher for the process according to the present invention (=23.4 wt %) as compared to a situation wherein the prior art process line-up is used (=14.4 wt %).

1. A process to prepare base oils from a Fischer-Tropsch synthesis product comprising

(a) separating a Fischer-Tropsch synthesis product into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii); (b) subjecting the base oil precursor fraction (ii) to a catalytic hydroisomerisation step in the presence of a catalyst comprising a binder, zeolite Beta and a Group VIII metal and a catalytic dewaxing step in the presence of a catalyst comprising a binder, a medium pore size zeolite and a Group VIII hydrogenation component to yield one or more base oil grades;

(c) subjecting the heavy ends fraction (iii) to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii); and

(d) subjecting a high boiling fraction (v) of fraction (iv) to a catalytic hydroisomerisation and catalytic dewaxing process to yield one or more base oil grades.

2. The process according to claim 1, wherein the heavy ends fraction (iii) has an initial boiling point of between 500 and 600° C.

3. The process according to claim 1, wherein the medium pore size zeolite in step (b) is selected from the group consisting of mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 or ZSM-48 and combinations of said zeolites.

4. The process according to claim 3, wherein the medium pore size zeolite in step (b) is ZSM-48.

5. The process according to claim 1, wherein the hydroisomerisation in step (b) is performed in the presence of a catalyst comprising a binder, zeolite Beta and platinum and a catalytic dewaxing step in the presence of a catalyst comprising a binder, a medium pore size zeolite and platinum.

6. The process according to claim 1, wherein step (c) is performed as a hydrocracking/hydroisomerisation process making use of an amorphous catalyst comprising an acidic functionality and a hydrogenation/dehydrogenation functionality.

7. The process according to claim 1, wherein the effluent of step (c) is provided to step (a), such that in effect steps (b) and (d) take place simultaneously.

8. A process to prepare base oils from a Fischer-Tropsch synthesis product by comprising

- (a) separating a Fischer-Tropsch synthesis product into a fraction (i) boiling in the middle distillate range and below, a heavy ends fraction (iii) and an intermediate base oil precursor fraction (ii) boiling between fraction (i) and fraction (iii);
- (b) subjecting the base oil precursor fraction (ii) to a catalytic hydroisomerisation step in the presence of a catalyst comprising a binder, zeolite Beta and a Group VIII metal and a catalytic dewaxing step in the presence of a catalyst comprising a binder, a medium pore size zeolite

- and a Group VIII hydrogenation component to yield one or more base oil grades; and
 - (c) subjecting the heavy ends fraction (iii) to a conversion step to yield a fraction (iv) boiling below the heavy ends fraction (iii) and recycling the high boiling fraction (v) of fraction (iv) boiling in the base oil range to step (b).
- 9.** The process according to claim **8**, wherein the fraction boiling above fraction (v) of fraction (iv) is recycled to step (c).

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