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# (54) Process to prepare base oil and gas oil

(57) A process for preparing gas oil and base oil by subjecting a part of a Fischer-Tropsch product to hydroconversion/hydroisomerisation at a conversion in the range of between 50 and 90 wt%, a hydrogen partial pressure between 45 and 75 bara, a temperature between 280 and 425 °C, using a catalyst comprising Pt and/or Pd, ASA, and no or hardly any zeolite;
subjecting another part of the Fischer-Tropsch product to hydroconversion/hydroisomerisation at a conversion between 30 and 60 wt%, a hydrogen partial pressure between 20 and 55 bara, a temperature between 175 and 375 °C, using a catalyst comprising Pt and/or Pd, ASA, and 0.1-15 wt% wt% zeolite;
distilling a fraction boiling in the gas oil range, a fraction boiling in the distillate base oil range, and a heavier fraction, from a combination the products of the hydroconversion/hydroisomerisation steps;
recycling at least a part of the heavier fraction; performing a pour point reducing step on the fraction boiling in the distillate base oil range.

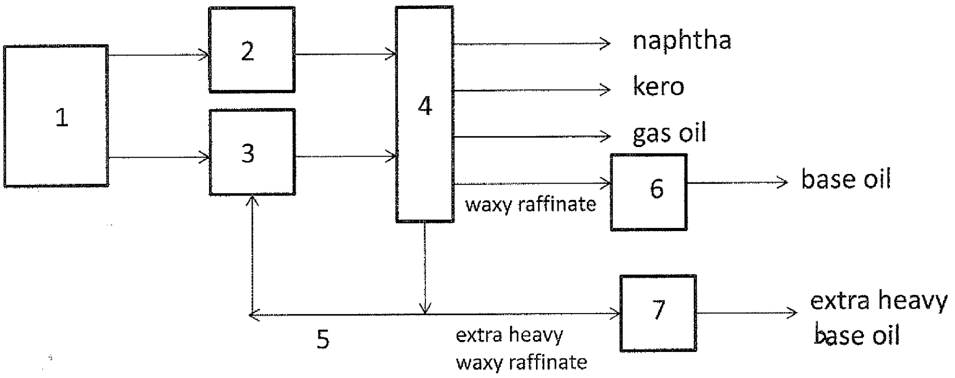

Fig. 1. TS2757

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## Description

### Field of the Invention

**[0001]** The invention is directed to a process to prepare base oil and gas oil from a Fischer-Tropsch product.

### Background of the Invention

**[0002]** WO02070629A1 describes a process to prepare a gas oil product and a base oil product from a Fischer-Tropsch product by performing hydroconversion/hydroisomeri sation and isolation of a gas oil fraction and a residue from the obtained cracked effluent. The residue is further distilled to obtain a distillate fraction boiling between 370 and 510 °C. This fraction boiling between 370 and 510 °C is subjected to catalytic dewaxing to obtain various base oil grades.

**[0003]** US20080314800A1 discloses a process to prepare a base oil product from a Fischer-Tropsch product by performing hydroconversion/hydroisomerisation and distillation. One part of a Fischer-Tropsch product is subjected to hydroconversion/hydroisomerisation at a certain conversion, preferably a conversion between 30 and 60%. Another part of the Fischer-Tropsch product is subjected to hydroconversion/hydroisomerisation at a higher conversion. This conversion is at least 5% higher, and preferably is a conversion between 50 and 95%. Preferably both hydroconversions are performed with the same type of catalyst. The conversion level may be adjusted by varying the temperature. With two hydroconversion reactors operating in parallel at different conversion levels a higher combined waxy raffinate yield is obtained as compared to the waxy raffinate yield of a single reactor operating at a conversion level which is the average of the conversion levels of the two reactors.

**[0004]** WO2006067174A1 describes a process to prepare a gas oil product and a base oil product from a Fischer-Tropsch product by performing hydroconversion/hydroisomeri sation and distillation. A relatively light part of a Fischer-Tropsch product is subjected to hydroconversion/ hydroisomerisation, and a relatively heavy part of a Fischer-Tropsch product is subjected to hydroconversion/hydroisomerisation. This may be performed in two hydroconversion reactors operating in parallel. Preferably the reactors have the same type of catalyst. The conversion may be the same or different. For the light part the conversion preferably is between 50 and 90%. For the heavy part the conversion preferably is between 30 and 60%. The light part of a Fischer-Tropsch product results in a higher gas oil yield and the heavy part results in a higher waxy raffinate yield.

**[0005]** The object of the present invention is to optimise the yield to gas oils and the yield to base oils from a Fischer-Tropsch product.

### Summary of the Invention

**[0006]** The present invention provides a process for preparing gas oil and base oil from a Fischer-Tropsch product, said process comprising the following steps:

(a) providing a Fischer-Tropsch product;
(b) subjecting a part of the Fischer-Tropsch product of step (a) to hydroconversion/hydroisomerisation

- at a conversion in the range of between 50 and 90 wt%, preferably between 50 and 80 wt%, more preferably between 50 and 70 wt%,
- a hydrogen partial pressure in the range of between 45 and 75 bara, preferably between 50 and 70 bara,
- a temperature in the range of between 280 and 425 °C, preferably between 325 and 400 °C,
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and less than 0.1 wt% zeolite, preferably less than 0.01 wt% zeolite, more preferably no zeolite;

(c) subjecting another part of the Fischer-Tropsch product of step (a) to hydroconversion/hydroisomerisation

- at a conversion in the range of between 30 and 60 wt%, preferably between 30 and 45 wt%, whereby the conversion in step (c) is at least 5 wt% lower as compared to the conversion in step (b),
- a hydrogen partial pressure in the range of between 20 and 55 bara, preferably between 30 and 50 bara, whereby the hydrogen partial pressure in step (c) is at least 5 bara, preferably at least 10 bara lower than the hydrogen partial pressure in step (b),
- a temperature in the range of between 175 and 375 °C, preferably between 250 and 375 °C, whereby the temperature in step (c) is at least 10 °C lower, preferably at least 20 °C lower than the temperature in step (b),
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and 0.1-15 wt% wt% zeolite, preferably 0.1-15 wt% zeolite beta;

(d) isolating by means of distillation:

- a fraction boiling in the gas oil range,
- a fraction boiling in the distillate base oil range, and
- a fraction heavier than the fraction boiling in the distillate base oil range, said fraction preferably comprising at least 50 wt% of material boiling above 540 °C,

from a combination of at least a part of the reaction product obtained in step (b) and at least a part of the reaction product obtained in step (c);

(e) recycling at least a part of the fraction heavier than the fraction boiling in the distillate base oil range to step (c);
(f) performing a pour point reducing step on at least a part of the fraction boiling in the distillate base oil range.

**[0007]** Applicants found that by the process of the present invention it is possible to optimize the yield of gas oil, and to optimize the yield of the fraction boiling in the distillate base oil range and thus to the base oils which are obtained after subjecting the fraction boiling in the distillate base oil range to a pour point reducing step. The fraction boiling in the distillate base oil range is sometimes referred to as waxy raffinate fraction.

Brief description of the drawings

**[0008]**

Figure 1 shows a process scheme in which the process according to the present invention may be suitably be carried out.

Detailed description of the invention

**[0009]** The present invention provides a process for preparing gas oil and base oil from a Fischer-Tropsch product, said process comprising the following steps:

(a) providing a Fischer-Tropsch product;
(b) subjecting a part of the Fischer-Tropsch product of step (a) to hydroconversion/hydroisomerisation

- at a conversion in the range of between 50 and 90 wt%, preferably between 50 and 80 wt%, more preferably between 50 and 70 wt%,
- a hydrogen partial pressure in the range of between 45 and 75 bara, preferably between 50 and 70 bara,
- a temperature in the range of between 280 and 425 °C, preferably between 325 and 400 °C,
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and less than 0.1 wt% zeolite, preferably less than 0.01 wt% zeolite, more preferably no zeolite;

(c) subjecting another part of the Fischer-Tropsch product of step (a) to hydroconversion/hydroisomerisation

- at a conversion in the range of between 30 and 60 wt%, preferably between 30 and 45 wt%, whereby the conversion in step (c) is at least 5 wt% lower as compared to the conversion in step (b),
- a hydrogen partial pressure in the range of between 20 and 55 bara, preferably between 30 and 50 bara, whereby the hydrogen partial pressure in step (c) is at least 5 bara, preferably at least 10 bara lower than the hydrogen partial pressure in step (b),
- a temperature in the range of between 175 and 375 °C, preferably between 250 and 375 °C, whereby the temperature in step (c) is at least 10 °C lower, preferably at least 20 °C lower than the temperature in step (b),
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and 0.1-15 wt% wt% zeolite, preferably 0.1-15 wt% zeolite beta;

(d) isolating by means of distillation:

- a fraction boiling in the gas oil range,
- a fraction boiling in the distillate base oil range, and
- a fraction heavier than the fraction boiling in the distillate base oil range, said fraction preferably comprising at least 50 wt% of material boiling above 540 °C,

from a combination of at least a part of the reaction product obtained in step (b) and at least a part of the reaction product obtained in step (c);

(e) recycling at least a part of the fraction heavier than the fraction boiling in the distillate base oil range to step (c);
(f) performing a pour point reducing step on at least a part of the fraction boiling in the distillate base oil range.

**[0010]** Applicants found that by the process of the present invention it is possible to optimize the yield of gas oil as well as the yield of the fraction boiling in the distillate base oil range. As the yield of the fraction boiling in the distillate base oil range is optimised also the yield of the base oils, which are obtained after subjecting the fraction boiling in the distillate base oil range to a pour point reducing step, is optimised. The fraction boiling in the distillate base oil range is sometimes referred to as waxy raffinate fraction.

**[0011]** The Fischer-Tropsch product which is provided in step (a) may be obtained from a single Fischer-Tropsch reactor in which the Fischer-Tropsch process is performed. Alternatively, the Fischer-Tropsch product which is provided in step a) may be obtained from two or more Fischer-Tropsch reactors in which the Fischer-Tropsch process is performed. The product(s) from the reactor(s) may be entire Fischer-Tropsch product stream(s) or a part thereof. Such a part may, for example, be split off, may be obtained by distillation, or may be obtained after removal of components such as water.

**[0012]** In case Fischer-Tropsch product provided in step (a) is obtained from two or more reactors, the product stream(s) of one or more reactors may be fed to step (b), while the product stream(s) from the other reactor(s) is bed to step (c). In case the product stream(s) of one or more reactors is heavier than the product stream(s) of the other reactor(s), preferably the lighter product stream(s) is/are fed to step (b), and the heavier product stream(s) is/are fed to step (c).

**[0013]** For example, in case Fischer-Tropsch product provided in step a) is obtained from two Fischer-Tropsch reactors, it is possible to feed the product from one reactor to step (b) and the product from the other reactor to step (c). In case the product of one reactor is heavier than the product of the other reactor, preferably the lighter product is fed to step (b), and the heavier product is fed to step (c).

**[0014]** In case the Fischer-Tropsch product which is provided in step (a) is obtained from a single Fischer-Tropsch reactor, the product may be split after which one part is fed to step (b) and another part is fed to step (c).

**[0015]** In case the Fischer-Tropsch product which is provided in step (a) is obtained from a single Fischer-Tropsch reactor, the product may be distilled after which preferably a lighter fraction is fed to step (b), and a heavier fraction is fed to step (c).

**[0016]** In case the Fischer-Tropsch product which is provided in step (a) is obtained from two or more reactors, at least a part of the product streams of both or all reactors may be combined and in a subsequent step the combined product may be split after which one part is fed to step (b) and another part is fed to step (c).

**[0017]** In case the Fischer-Tropsch product which is provided in step (a) is obtained from two or more reactors, at least a part of the product streams of both or all reactors may be combined and in a subsequent step the combined product may be distilled after which a lighter fraction is fed to step (b), and a heavier fraction is fed to step (c).

**[0018]** The Fischer-Tropsch product provided in step (a) is a product directly obtained from a Fischer-Tropsch synthesis reaction, which product may optionally have been subjected to a distillation and/or hydrogenation step only.

**[0019]** The Fischer-Tropsch synthesis product can be obtained by well-known processes, for example the so-called commercial Slurry Phase Distillate technology of Sasol, the Shell Middle Distillate Synthesis Process or by the non-commercial "AGC-21" Exxon Mobil process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, US-A-4943672, US-A-5059299, WO-A-9934917 and WO-A-9920720. Most of these processes are carried out at temperatures between 200 and 280 °C, especially 210-260 °C. The catalyst contains often cobalt or iron, preferably cobalt. The pressure is suitably between 10 and 80 bar, especially between 20 and 65 bar. The reaction is usually carried out in a fix bed reactor or a slurry reactor.

**[0020]** A Fischer-Tropsch synthesis product typically comprises hydrocarbons having 1 to 100 and even more than 100 carbon atoms, e.g. up to 200 carbon atoms or occasionally even more. This hydrocarbon product will comprise normal paraffins, iso-paraffins, oxygenated products and unsaturated products. Paraffins and unsaturated product, especially olefins, more especially alpha-olefins, are the main constituents of the Fischer-Tropsch product. Depending on the actual reaction conditions, the amount of olefins may vary from 5 to 90 wt% of the total feed stream. The amount of iso-paraffins (and iso-olefins) also depends on the actual reaction conditions. Usually the amount of iso-compounds is up to 25 wt% of the total feed stream, suitably between 1 and 20 wt%, especially between 3 and 15 wt%. The amount of oxygenates is usually up till 10 wt% of the total feed stream, suitably between 0.5 and 6 wt%.

**[0021]** The Fischer-Tropsch product provided in step (a) suitably is the full $C_5$+ fraction of the Fischer-Tropsch process, i.e. no heavy compounds have been removed from the fraction. Other suitable products that may be provided in step (a) are the full $C_{12}$+ fraction of the Fischer-Tropsch process or the full $C_{18}$+ fraction, i.e. the 200 °C plus fraction or the 310 °C plus fraction of the Fischer-Tropsch process. Optionally also the fraction boiling above 380 °C, or even boiling above 750 °C, may be provided in step (a).

**[0022]** The Fischer-Tropsch product provided in step (a) preferably is the full high boiling fraction, i.e. no heavy compounds, e.g. $C_{21}$+ compounds, are removed from the high boiling fraction.

**[0023]** The Fischer-Tropsch product provided in step (a) preferably is relatively heavy. The relatively heavy Fischer-Tropsch product provided in step (a) preferably has at least 30 wt%, more preferably at least 50 wt%, and even more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product preferably is at least 0.2, more preferably at least 0.4 and even more preferably at least 0.55. Preferably the Fischer-Tropsch product comprises a $C_{20}$+ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor derived from the $C_{20}$ compounds and the $C_{40}$ compounds of the Fischer-Tropsch product stream) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955.

**[0024]** Preferably any compounds having 4 or less carbon atoms and any compounds having a boiling point in that range are separated from a Fischer-Tropsch synthesis product before the Fischer-Tropsch synthesis product is used in step (b) or (c).

**[0025]** A part of the Fischer-Tropsch product provided in step (a) is used in step (b) and another part is used in step (c).

**[0026]** The Fischer-Tropsch product provided in step

(a) may be simply split into two equal parts and the two parts are used as feed in steps (b) and (c). For the present invention, it is not essential that these two parts are of the same volume. For instance, 25-50 wt% of the total feed may go to step (b) and 75-50 wt% may go to step (c).

**[0027]** Furthermore, it may be envisaged that the Fischer-Tropsch product from one or more parallel operated Fischer-Tropsch synthesis reactor types, for example slurry bubble or multi-tubular reactors, are fed to step (b) while one or more other parallel operated Fischer-Tropsch reactor types provide the feed for step (c).

**[0028]** It may also be envisaged that all the products from all or almost all of the Fischer-Tropsch synthesis reactors are mixed at a so-called common header and that from this combined product the two feeds for step (b) and (c) may be obtained.

**[0029]** It is also part of this invention that in addition to steps (b) and (c), more parallel operated hydroconversion/hydrocracking reactors are present. It is understood that the Fischer-Tropsch product provided in step (a) will then be split over more than two feeds provided that at least two reactors operate at a different conversion according to the present invention.

**[0030]** The feed streams to step (b) and step (c) may be the same feed streams or different feed streams. Preferably each feed stream comprises at least 20 wt% of the feed stream of compounds boiling above 360 °C, more preferably at least 40 wt%, more preferably at least 60 wt%, still more preferably at least 85 wt%.

**[0031]** The feed for steps (b) and (c) may next to the Fischer-Tropsch product also comprise of mineral crude derived fractions and/or gas field condensates. These additional sulphur containing co-feeds are advantageous when a sulphided catalyst is used in steps (b) and (c). The sulphur in the feed will keep the catalyst in its sulphided form. The sulphur may be removed in a down stream treating unit or, in case the quantities are very low, become part of the product of the present invention.

**[0032]** In step (b) a part of the Fischer-Tropsch product of step (a) is subjected to hydroconversion/hydroisomerisa tion

- at a conversion in the range of between 50 and 90 wt%, preferably between 50 and 80 wt%, more preferably between 50 and 70 wt%,
- a hydrogen partial pressure in the range of between 45 and 75 bara, preferably between 50 and 70 bara,
- a temperature in the range of between 280 and 425 °C, preferably between 325 and 400 °C,
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and less than 0.1 wt% zeolite, preferably less than 0.01 wt% zeolite, more preferably no zeolite.

**[0033]** In step (c) a part of the Fischer-Tropsch product of step (a) is subjected to hydroconversion/hydroisomerisa tion

- at a conversion in the range of between 30 and 60 wt%, preferably between 30 and 45 wt%, whereby the conversion in step (c) is at least 5 wt% lower as compared to the conversion in step (b),
- a hydrogen partial pressure in the range of between 20 and 55 bara, preferably between 30 and 50 bara, whereby the hydrogen partial pressure in step (c) is at least 5 bara, preferably at least 10 bara lower than the hydrogen partial pressure in step (b),
- a temperature in the range of between 175 and 375 °C, preferably between 250 and 375 °C, whereby the temperature in step (c) is at least 10 °C lower, preferably at least 20 °C lower than the temperature in step (b),

  using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and 0.1-15 wt% wt% zeolite, preferably 0.1-15 wt% zeolite beta.

**[0034]** The catalyst used in step (b) comprises platinum and/or palladium, amorphous silica-alumina (ASA), and less than 0.1 wt% zeolite, preferably less than 0.01 wt% zeolite, more preferably no zeolite.

**[0035]** The catalyst used in step (c) comprises platinum and/or palladium, amorphous silica-alumina (ASA), and 0.1-15 wt% wt% zeolite, preferably 0.1-15 wt% zeolite beta.

**[0036]** For the catalyst used in step (b), as well as for the catalyst used in step (c), the platinum and/or palladium is preferably 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 ASA. If both platinum and palladium are present in the catalyst, the weight ratio of platinum to palladium in the catalyst may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5.

**[0037]** The catalyst used in step (b), and the catalyst used in step (c), each preferably 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 $m^2/g$ as determined by BET nitrogen adsorption, and a bulk density of between 0.4-1.0 g/ml. The catalyst support is amorphous silica-alumina with preferably between 5 and 96 wt% alumina, more preferably between 20 and 85 wt% alumina, calculated on the total weight of silica-alumina. The silica content as $SiO_2$ preferably is between 15 and 80 wt%, calculated on the total weight of silica-alumina.

**[0038]** 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.

**[0039]** A catalyst suitable for step (b) has, for example, been described in EP0532117A and in WO02/070628.

**[0040]** A catalyst suitable for step (c) has, for example, been described in WO2011064236.

**[0041]** The catalyst used in step (b), and the catalyst used in step (c), each preferably is prepared by co-impregnating the platinum and/or palladium from solutions onto the support, followed by drying and optionally calcination. Drying may, for example, be performed in an inert atmosphere or in air at a temperature of between 100 and 150 °C. Calcination may, for example, be performed in an inert atmosphere or in air at a temperature of between 200 and 550 °C.

**[0042]** The catalyst used in step (b) and the catalyst used in step (c) are preferably reduced before being used. The metallic catalyst may be obtained as an oxidic or a prereduced catalyst. The above catalysts which are used in a sulphided form may be obtained in an oxidic, a pre-sulphided or a presulphurised form. Preferably the start-up procedure of the catalyst manufacturer is followed. Pre-reducing the catalyst for use in a metallic form may also be achieved *in situ* by reducing the catalyst by contacting with hydrogen. Preferably the contacting is achieved by contacting the catalyst at an elevated temperature with hydrogen in e.g. nitrogen mixture stream. More preferably the hydrogen content is increased over time and/or the temperature is gradually increased. A skilled person will be able to achieve a successful reduction of the catalyst by applying generally applied skills.

**[0043]** In step (b) and (c) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure.

**[0044]** In step (b) the hydrogen partial pressure is in the range of between 45 and 75 bara, preferably between 50 and 70 bara, and the temperature is in the range of between 280 and 425 °C, preferably between 325 and 400 °C.

**[0045]** In step (c) the hydrogen partial pressure is in the range of between 20 and 55 bara, preferably between 30 and 50 bara, whereby the hydrogen partial pressure in step (c) is at least 5 bara, preferably at least 10 bara lower than the pressure in step (b). In step (c) the temperature is in the range of between 175 and 375 °C, preferably between 250 and 375 °C, whereby the temperature in step (c) is at least 10 °C lower, preferably at least 20 °C lower than the temperature in step (b).

**[0046]** In steps (b) and (c), the hydrocarbon feed may be provided at a weight hourly space velocity of from 0.1 to 5 kg/1/hr (mass feed/volume catalyst bed/time), preferably higher than 0.5 kg/1/hr and more preferably lower than 2 kg/1/hr. In steps (b) and (c), hydrogen may be supplied at a ratio of hydrogen to hydrocarbon feed from 100 to 5000 Nl/kg and preferably from 250 to 2500 Nl/kg.

**[0047]** Steps (b) and (c) are preferably performed in reactors provided with beds of the heterogeneous catalysts as described above. The reactors may have the same size or a different size.

**[0048]** The conversion in steps (b) and (c) is defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C. The feed as used in this definition is the total hydrocarbon feed fed to steps (b) and (c), thus including any optional recycle feeds.

**[0049]** In step (b) the hydroconversion/hydroisomerisation is performed at a conversion in the range of between 50 and 90 wt%, preferably between 50 and 80 wt%, more preferably between 50 and 70 wt%.

**[0050]** In step (c) the hydroconversion/hydroisomerisation is performed at a conversion in the range of between 30 and 60 wt%, preferably between 30 and 45 wt%, whereby the conversion in step (c) is at least 5 wt% lower as compared to the conversion in step (b).

**[0051]** The conversion in step (c) is at least 5 wt% lower as compared to the conversion in step (b), preferably at least 10 wt% lower, more preferably at least 15 wt% lower. The conversion in step (c) preferably is at most 35 wt% lower as compared to the conversion in step (b), more preferably at most 30 wt% lower, even more preferably at most 25 wt% lower.

**[0052]** Prior to the hydroconversion/hydroisomerisation steps (b) and (c) the feed may optionally be subjected to a mild hydrotreatment step, in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Preferably the hydrogenation step reduces the level of oxygenates to below 150 ppm as measured by infrared absorption spectrometry and reduces the level of unsaturated compounds to below the detection limit of the infrared absorption spectrometry.

**[0053]** Such a hydrotreatment is for example described in EP668342B. 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%, even more preferably less than 5 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. After such a mild hydrotreatment, lower boiling compounds, having four or less carbon atoms and other compounds boiling in that range, will preferably be removed from the effluent before it is used in step (a). Examples of suitable catalysts are noble metal catalyst as for example platinum based hydrogenation catalysts or non-noble catalysts such as high content nickel catalysts.

**[0054]** In step (d) a combination of at least a part of the reaction product obtained in step (b) and at least a part of the reaction product obtained in step (c) is subjected to distillation. By means of distillation a fraction boiling in the gas oil range, a fraction boiling in the distillate base oil range, and a fraction heavier than the fraction boiling in the distillate base oil range are isolated.

**[0055]** A fraction boiling in the gas oil range is defined as a fraction boiling in the range between 180 and 400 °C, preferably in the range between 190 and 380 °C.

**[0056]** A fraction boiling in the distillate base oil range is defined as a fraction having a T10wt% boiling point of between 200 and 520 °C, preferably between 300 and 500 °C, and having a T90wt% boiling point between 400 and 650°C, preferably between 450 and 600°C.

**[0057]** A fraction heavier than a fraction boiling in the distillate base oil range is defined as a fraction having a

T5wt% boiling point of between 400 and 650 °C, preferably between 450 and 600 °C. This fraction preferably comprises at least 50 wt% of material boiling above 540 °C. This fraction preferably has a pour point of below 150 °C, more preferably below 130 °C, even more preferably below 110 °C.

**[0058]** The TxxWt%, wherein xx is between 1 and 98, boiling points in this context are the xxth percentiles of the true boiling point distribution as measured by a gas chromatographic simulation as in IP 480-02.

**[0059]** In step (e) at least a part of the fraction heavier than the fraction boiling in the distillate base oil range is recycled to step (c).

**[0060]** Another part of the fraction heavier than the fraction boiling in the distillate base oil range may be subjected to a pour point reducing step. The fraction heavier than the fraction boiling in the distillate base oil range may also be referred to as extra heavy waxy raffinate. In case a part of the extra heavy waxy raffinate is subjected to a pour point reducing step, for example to catalytic dewaxing, extra heavy base oil can be obtained.

**[0061]** In step (f) a pour point reducing step is performed on at least a part of the fraction boiling in the distillate base oil range. Hereby base oils can be obtained.

**[0062]** The pour point reducing step of step (f) may, for example, be a solvent dewaxing treatment or a catalytic pour point reducing treatment step.

**[0063]** With a pour point reducing treatment is understood every process wherein the pour point, as measured by ASTM D 97, of the base oil is reduced by more than 10 °C, preferably more than 20 °C, more preferably more than 25 °C.

**[0064]** Preferably the pour point reducing step of step (f) is a catalytic pour point reducing treatment step such as catalytic dewaxing.

**[0065]** The catalytic pour point reducing process can be performed by any process wherein, in the presence of a catalyst and hydrogen the pour point of the fraction after processing is improved, as specified above. Suitable dewaxing catalysts are heterogeneous catalysts comprising a molecular sieve optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Preferred molecular sieves are intermediate pore size zeolites. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites and other aluminosilicate materials are zeolite beta mordenite, ZSM-5, ZSM-12, ZSM-22, ZSM-23, MCM-68, SSZ-32, ZSM-35 and ZSM-48. Another preferred group of molecular sieves are the silica-aluminophosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal, or mixtures of said metals. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Pt/Zeolite beta, PtPd/Zeolite beta, Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48, Pt/ZSM-12 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

**[0066]** The crystallite size of the aluminosilicate zeolite 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 as measured by XRD line broadening. The critical size to measure is the length of the crystallite in the direction of the pores.

**[0067]** The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, 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: silica, 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 silica, zirconia, titanium dioxide, germanium dioxide, and mixtures of two or more of these of which examples are listed above. The most preferred binder is silica.

**[0068]** A preferred class of dewaxing catalysts comprise intermediate pore size zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above. Preferably the zeolite has been subjected to a dealumination treatment such as steaming. More preferably the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. A preferred surface 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 US-A-5157191 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.

**[0069]** 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, preferably from 15 to 100 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/1/hr), suitably from 0.2 to 5 kg/1/hr, more suitably from 0.5 to 3 kg/1/hr and hydrogen to oil ratios in the range of from 100 to 2,000 normal litres of hydrogen per litre of oil. By varying the temperature between 280 and 380 °C at a pressure of between 15-100 bars, in the catalytic dewaxing step it has been found possible to prepare base oils having different pour points varying from suitably lower than below the lowest measurable pour point, which is around -60 °C to up to 0 °C.

**[0070]** After performing the pour point reducing treatment and if required lower boiling compounds formed during said treatment are suitably removed, preferably by means of a vacuum distillation, flashing step or a stripping step or combinations of said steps. One or more base oils grades may be obtained by distillation of the dewaxed product. Preferably such a distillation is performed in one distillation step performed under low pressure.

**[0071]** The base oil products may be blended with other types of base oils, for example with base oils obtained from a mineral petroleum crude source or base oils as prepared by means of oligomerisation of lower olefins, for example $C_3$-$C_{12}$ olefins and/or from $C_4$-$C_{12}$ di-olefins. Preferably these other base oils are co-fed to the pour point reducing step with the fractions obtained in step (c). In this manner a base oil having just the targeted pour point, viscosity and Noack volatility is advantageously obtained.

**[0072]** The base oil products preferably comprise of at least a medium grade base oil having a kinematic viscosity at 100 °C of between 3.0 and 5.6 cSt and a heavy base oil grade having a kinematic viscosity at 100 °C of greater than 6 cSt. The upper viscosity limit will depend on the fractions of heavy Fischer-Tropsch compounds that are still present in the feed to the catalytic dewaxing unit and may range to 30 cSt at 100 °C. The Noack volatility of the medium grade base oil is preferably between 9 and 40% more preferably between 9 and 25%. Typical distillation operations will be suited to obtain base oils having the current volatility specifications of base oils in general. The viscosity index may range from 110 for the lower viscosity grades to up to 170 for the more viscous grades. The viscosity index (VI) will also depend on the severity of the dewaxing step wherein lower VI values are found for base oils having a lower pour point.

## Detailed description of the Figure

**[0073]** Figure 1 shows a process scheme in which the process according to the present invention may be suitably be carried out.

**[0074]** A Fischer-Tropsch product is provided, for example by a Fischer-Tropsch reactor (1). A part of the Fischer-Tropsch product is subjected to hydroconversion/hydroiso merisation in reactor (2) at a conversion in the range of between 50 and 90 wt%, a hydrogen partial pressure in the range of between 45 and 75 bar a, and a temperature in the range of between 280 and 425 °C, using a Pt comprising catalyst with a non-zeolitic ASA support. Another part of the Fischer-Tropsch product is subjected to hydroconversion/hydroisomerisation in reactor (3) at a conversion in the range of between 30 and 60 wt%, a hydrogen partial pressure in the range of between 20 and 55 bar a, and a temperature in the range of between 175 and 375 °C, using a Pt comprising catalyst with an ASA support comprising zeolite beta. The products of reactors 2 and 3 are combined and distilled in distillation column (4). The products obtained by the distillation in distillation column (4) are naphtha, kerosene, gas oil, waxy raffinate and extra heavy waxy raffinate. A part of the extra heavy waxy raffinate is recycled to reactor (3). Waxy raffinate, which is a fraction boiling in the distillate base oil range, is subjected to catalytic dewaxing in reactor (6) and base oil is obtained. Extra heavy waxy raffinate, which is a fraction heavier than a fraction boiling in the distillate base oil range, is subjected to catalytic dewaxing in reactor (7) and extra heavy base oil is obtained.

## Claims

**1.** A process for preparing gas oil and base oil from a Fischer-Tropsch product, said process comprising the following steps:

(a) providing a Fischer-Tropsch product;
(b) subjecting a part of the Fischer-Tropsch product of step (a) to hydroconversion/hydroisomerisation

- at a conversion in the range of between 50 and 90 wt%, preferably between 50 and 80 wt%, more preferably between 50 and 70 wt%,
- a hydrogen partial pressure in the range of between 45 and 75 bara, preferably between 50 and 70 bara,
- a temperature in the range of between 280 and 425 °C, preferably between 325 and 400 °C,
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and less than 0.1 wt% zeolite, preferably less than 0.01 wt% zeolite, more preferably no zeolite;

(c) subjecting another part of the Fischer-Tropsch product of step (a) to hydroconversion/hydroisomerisation

- at a conversion in the range of between 30 and 60 wt%, preferably between 30 and 45 wt%, whereby the conversion in step (c) is at least 5 wt% lower as compared to the conversion in step (b),
- a hydrogen partial pressure in the range

of between 20 and 55 bara, preferably between 30 and 50 bara, whereby the hydrogen partial pressure in step (c) is at least 5 bara, preferably at least 10 bara lower than the hydrogen partial pressure in step (b),
- a temperature in the range of between 175 and 375 °C, preferably between 250 and 375 °C, whereby the temperature in step (c) is at least 10 °C lower, preferably at least 20 °C lower than the temperature in step (b),
- using a catalyst comprising a platinum and/or palladium, an amorphous silica-alumina (ASA), and 0.1-15 wt% wt% zeolite, preferably 0.1-15 wt% zeolite beta;

(d) isolating by means of distillation:

- a fraction boiling in the gas oil range,
- a fraction boiling in the distillate base oil range, and
- a fraction heavier than the fraction boiling in the distillate base oil range, said fraction preferably comprising at least 50 wt% of material boiling above 540 °C,

from a combination of at least a part of the reaction product obtained in step (b) and at least a part of the reaction product obtained in step (c);

(e) recycling at least a part of the fraction heavier than the fraction boiling in the distillate base oil range to step (c);
(f) performing a pour point reducing step on at least a part of the fraction boiling in the distillate base oil range,
whereby the conversion in steps (b) and (c) is the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C.

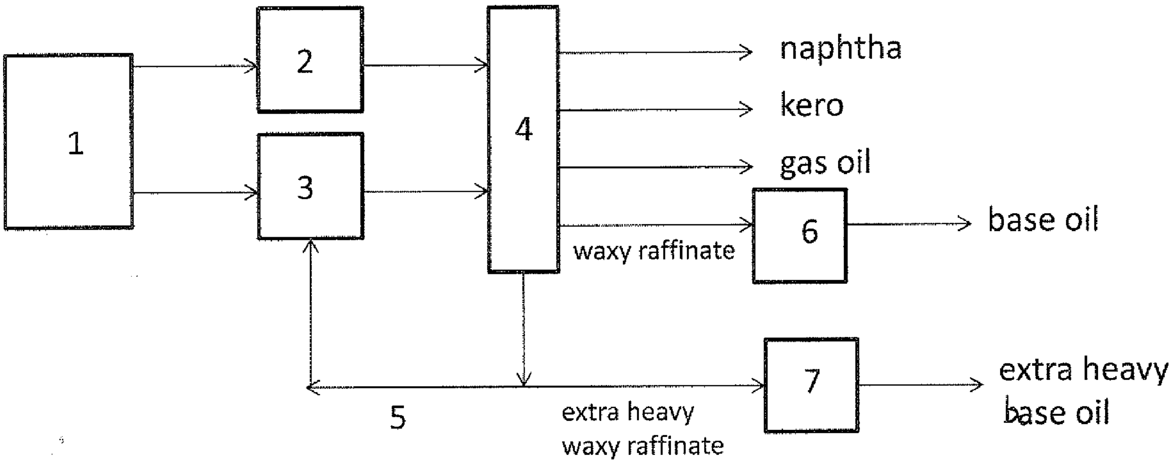
1
2
3
4
naphtha
kero
gas oil
waxy raffinate
6
base oil
5
extra heavy
waxy raffinate
7
extra heavy
base oil

Fig. 1. TS2757

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## EUROPEAN SEARCH REPORT

Application Number
EP 12 19 7722

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