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# (54) PROCESS TO PREPARE FISCHER-TROPSCH DERIVED MIDDLE DISTILLATES AND BASE OILS

(57) The invention provides a process to prepare at least middle distillates and base oils from a Fischer-Tropsch derived feedstock, by

(a) providing a Fischer-Tropsch derived feedstock containing nitrogen through addition of a nitrogen containing compound selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring to a Fischer-Tropsch reactor;

(b) subjecting the feedstock of step (a) to a hydroprocess-

ing step in the presence of one or more catalysts to obtain a first mixture comprising one or more middle distillate fractions and a first residual fraction and naphtha fraction; (c) separating the first mixture as obtained in step (b) by means of atmospheric distillation into one or more middle distillate fractions, a first residual fraction and a naphtha fraction;

(d) separating the first residual fraction by means of vacuum distillation into at least a distillate base oil fraction and a second residual fraction.

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#### Description

#### FIELD OF THE INVENTION

5 [0001] The present invention is directed to a process to prepare Fischer-Tropsch derived middle distillates and base oils.

#### BACKGROUND TO THE INVENTION

**[0002]** Earlier studies have shown that catalysts used to convert Fischer-Tropsch derived feedstock into final products require low levels of heteroatoms for efficient operation. The key heteroatoms that are indicated to be controlled to low levels are nitrogen and oxygen. Nitrogen is mentioned to be the most serious catalyst poison, while oxygen is a lesser concern. The presence of nitrogen in a feedstock is claimed to cause the reactions to be performed at higher than desired hydroprocessing reactor temperatures, with a serious reduction in the yield of valuable products. In US 6,635,171 B2 for example is disclosed a process to upgrade nitrogen-containing Fischer-Tropsch products. US 6,635,171 B2 discloses that hydrotreating of high nitrogen-content waxy Fischer-Tropsch products prior to catalytic hydroisomerization improves activity of the dewaxing catalyst and improves lubes yields.

**[0003]** A problem of the process as disclosed in US 6,635,171 B2 is that although the catalytic activity of the dewaxing catalyst and the obtained lubes yield is achieved, extra process steps (purification, monitoring and adjustment) need to be followed to reduce the nitrogen content of Fischer-Tropsch products used as feedstock for the hydrotreating step, below a threshold value. Moreover, if the nitrogen content of the purified Fischer-Tropsch product increases (monitoring step), the severity of the hydrotreating step (purification step) must be increased to compensate for this increase (adjustment). To obtain lubes with the process in US6,635,171 B2 a lot of extra steps are necessary and therefore making that process complex and capex intensive.

#### SUMMARY OF THE INVENTION

[0004] It is an object of the invention to solve or minimize at least of one of the above problems.

**[0005]** It is a further object of the invention to provide a hydroprocessing process in which the presence of nitrogen containing compounds does not affect the activity of the catalyst and therefore does not result in the reduction in the yield of valuable products, such as base oils.

**[0006]** Another object of the invention is to provide an efficient method for preparation of high yield middle distillates with excellent cold flow properties and a high yield of base oils.

**[0007]** One of the above or other objects may be achieved according to the present invention by providing a process to prepare at least middle distillates and base oils from a Fischer-Tropsch derived feedstock, by

- (a) providing a Fischer-Tropsch derived feedstock containing nitrogen through addition of a nitrogen containing compound selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring to a Fischer-Tropsch reactor;
- (b) subjecting the feedstock of step (a) to a hydroprocessing step in the presence of one or more catalysts to obtain a first mixture comprising one or more middle distillate fractions and a first residual fraction and naphtha fraction;
- (c) separating the first mixture as obtained in step (b) by means of atmospheric distillation into one or more middle distillate fractions, a first residual fraction and a naphtha fraction; and
- (d) separating the first residual fraction by means of vacuum distillation into at least a distillate base oil fraction and a second residual fraction.

[0008] It has now surprisingly been found according to the present invention that in the presence of nitrogen containing compounds high yield of middle distillates with excellent cold flow properties and a high yield of base oils can be prepared.

[0009] An advantage of the present invention is that although the catalyst activity is affected by the presence of the nitrogen containing compounds and hence the catalytic reaction takes place at a higher operating temperature, no negative impact on the yield profile is observed but surprisingly higher yields are obtained.

**[0010]** A further advantage of the present invention is that not only the presence of nitrogen containing compounds but also the addition of an increasing amount of added nitrogen containing compounds enacts that base oils and gasoil are obtained with better properties.

# 55 DETAILED DESCRIPTION OF THE INVENTION

**[0011]** In the step (a) of the process according to the present invention a Fischer-Tropsch derived feedstock is provided containing nitrogen through addition of a nitrogen containing compound selected from ammonia, HCN, NO, amines,

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nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring to a Fischer-Tropsch reactor.

[0012] The Fischer-Tropsch derived feedstock is a product derived from a Fischer-Tropsch process. Fischer-Tropsch product is known in the art. By the term "Fischer-Tropsch product" is meant a synthesis product of a Fischer-Tropsch process. In a Fischer-Tropsch process synthesis gas is converted to a synthesis product. Synthesis gas or syngas is a mixture of hydrogen and carbon monoxide that is obtained by conversion of a hydrocarbonaceous feedstock. Suitable feedstocks include natural gas, crude oil, heavy oil fractions, coal, biomass and lignite. A Fischer-Tropsch product may also be referred to as GTL (Gas-to-Liquids) product. The preparation of a Fischer-Tropsch product has been described in e.g. WO2003/070857.

10013] The Fischer-Tropsch product of the Fischer-Tropsch process is usually separated into a water stream, a gaseous stream comprising unconverted synthesis gas, carbon dioxide, inert gases and C1 to C2, and a C3+ product stream by distillation. Commercially available equipment can be used. The distillation may be carried out at atmospheric pressure, but also reduced pressure may be used. By Fischer-Tropsch product stream in step (a) is preferably meant the C3+ product stream.

[0014] Preferably, the Fischer-Tropsch feedstock comprises 81% of compounds boiling above 370 °C and 49% of compounds boiling above 540 °C.

**[0015]** In one embodiment the Fischer-Tropsch derived feedstock as provided in step (a) is prepared by adding to a gaseous feed stream comprising hydrogen and carbon monoxide a nitrogen containing compound to obtain a mixture wherein the nitrogen containing compound is selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring.

Suitably, to the gaseous feed stream a nitrogen-containing compound is added such that the nitrogen-containing compound is present in the gaseous feed stream in a concentration of up to 10 ppmV.

**[0016]** Preferably, the nitrogen-containing compound is added to the gaseous feed stream such that the nitrogen-containing compound is present in the gaseous feed stream in a concentration in the range of 0.05 to 10 ppmV.

**[0017]** The obtained mixture is then fed to a Fischer-Tropsch reactor to obtain a Fischer-Tropsch feedstock containing nitrogen through the addition of a nitrogen containing compound selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring to the gaseous feed stream. Typically, it is known by the skilled person in the art that at least ammonia and amines are made in the Fischer-Tropsch reactor.

30 Preferably, the Fischer-Tropsch product stream as provided in step (a) comprises paraffins having from 3 to 300 carbon atoms.

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[0018] In a preferred embodiment the Fischer-Tropsch derived feedstock as provided in step (a) is prepared by adding to a Fischer-Tropsch product stream as obtained from a Fischer-Tropsch process a nitrogen containing compound selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring. Preferably, the Fischer-Tropsch product stream to which the nitrogen containing compound is added comprises paraffins having from 5 to 300 carbon atoms.

**[0019]** Suitably, the nitrogen containing compound (expressed as concentration of Nitrogen (N)) added to the Fischer-Tropsch product is in the range from 0.1 to 20 ppmw, preferably from 0.2 to 17 ppmw, more preferably from 0.3 to 14 ppmw, even more preferably from 0.4 to 12 ppmw.

40 Preferably, the nitrogen is present in the Fischer-Tropsch feedstock of step (a) in a concentration between 0.5 and 10 ppmw.

**[0020]** Preferably, the nitrogen containing compound comprises amines. More preferably, the amine is decylamine. The amount of decylamine added to the Fischer-Tropsch product is in the range of from 1 to 225 ppmw, preferably from 2 to 191 ppmw, more preferably from 3 to 157 ppmw, even more preferably from 4 to 135 ppmw, most preferably from 60 to 112 ppmw. These ranges are equivalent to the following concentrations of nitrogen (N) in the range of from 0.1-20 ppmw.

**[0021]** In step (b) of the process according to the present invention the feedstock of step (a) is subjected to a hydroprocessing step in the presence of one or more catalysts to obtain a first mixture comprising one or more middle distillate fractions and a first residual fraction and naphtha fraction.

**[0022]** Hydroprocessing in step (b) may take place in a heavy paraffin conversion unit. In this unit, preferably in the presence of one or more catalysts of step (b) both hydrocracking and hydroisomerization takes place. In step (b), the Fischer-Tropsch feedstock is contacted in the presence of hydrogen, at a pressure in the range of 20 to 100 barg and at a temperature between 250 and 400°C. Preferably, step (b) takes place at a pressure in the range of from 30 to 70 barg and at a temperature between 300 and 400°C.

Hydrocracking/hydroisomerization processes are known in the art and therefore not discussed here in detail. Hydrocracking/hydroisomerization and the effect of hydrocracking/hydroisomerization conditions on the amount of isomerised product are for example described in Chapter 6 of "Hydrocracking Science and Technology", Julius Scherzer; A. J. Cruia, Marcel Dekker, Inc, New York, 1996, ISBN 0-8247-9760-4.

[0023] Step (b) takes place in the presence of one or more catalysts.

**[0024]** Preferably, one or more catalyst of step (b) comprises a Group VIII noble metal supported on an amorphous acidic carrier. Typically, the one or more catalysts of step (b) comprise a Group VIII noble metal supported on an amorphous acidic carrier as a hydroprocessing catalyst.

[0025] Preparation of the hydroprocessing catalyst utilized in step (b) is for example described in WO2011/064236.

**[0026]** Preferably, one or more catalyst of step (b) comprises a Group VIII metal and a medium pore size molecular sieve. Typically, the one or more catalysts of step (b) comprising a Group VIII metal and a medium pore size molecular sieve is a catalytic dewaxing catalyst.

[0027] Preparation of the dewaxing catalysts utilized in step (b) is for example described in WO2015/063213.

**[0028]** In another embodiment, step (b) takes place in the presence of a stacked bed of catalysts. Preferably, the stacked bed of catalyst are two different catalysts in series, wherein hydroprocessing of the Fischer-Tropsch feedstock of step (b) takes place by contacting the Fischer-Tropsch feedstock with a first catalyst having hydrocracking and hydroisomerising activity and then with a second catalyst having hydrocracking and hydroisomerising activity, wherein the second catalyst is more active in hydroisomerisation and less active in hydrocracking compared to the first catalyst. Typically, the first catalyst comprises a Group VIII noble metal supported on an amorphous acidic carrier and the second

catalyst comprises a Group VIII metal and a medium pore size molecular sieve.

**[0029]** Preparation of the catalysts used in the stacked bed in step (b) is for example described in WO2015/063213 and WO2011/064236.

[0030] In step (c) of the process according to the present invention the first mixture as obtained in step (b) is separated by means of atmospheric distillation into one or more middle distillate fractions, a first residual fraction and a naphtha fraction. The one or more middle distillate fractions may comprise a single middle distillate fraction, for example a single fraction having a majority of components, for instance 95vol% or greater, boiling in the range of from 150°C to 400°C. This single fraction is preferably a wide range gasoil. Preferably, in step (b) at least a gasoil fraction is obtained. The gasoil fraction will usually contain a majority of components having boiling points within the typical diesel fuel ("gasoil") range, i.e. from about 150 to 400°C or from 170 to 370°C. It will suitably have a 90 vol % distillation temperature of from 300 to 370°C according to ASTM D86. Said gasoil fraction is typically a wide range heavy gasoil fraction.

**[0031]** Although the catalyst activity is affected by the presence of the nitrogen containing compounds in step (b) of the process according to the present invention and hence the catalytic reaction takes place at a higher operating temperature, no negative impact on the yield profile is observed but surprisingly higher yields in middle distillates are obtained compared to a reaction without the presence of nitrogen containing compound. In addition, the cloud point of the gasoil fraction improves upon addition of an increasing amount of nitrogen containing compound compared to the cloud point of the gasoil fraction reached without the addition of nitrogen containing compound. The cloud point of the gasoil fraction (wide range or heavy gasoil) is preferably below -10°C, preferably between -15 and -35°C and is therefore suitable for the production of Nordic/and or arctic grade diesel and/or diesel blending components.

Optionally, the wide range gasoil can be distilled into a kerosene fraction and a heavy gasoil fraction.

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**[0032]** Suitably the kerosene fraction as obtained in step c) has a freezing point below -40°C. In this way, the kerosene fraction as obtained in step c) according to the process of the present invention has cold flow properties which properties make the kerosene fraction suitable as aiet-A or even jet-Al blending component.

**[0033]** The first residual fraction comprises compounds boiling above the middle distillate boiling range. Suitably, the first residual fraction is a fraction of which at least 95 wt.% has a boiling point above 330°C.

**[0034]** In step (d) of the process of the present invention the first residual fraction is separated by means of vacuum distillation into at least a distillate base oil fraction and a second residual fraction. The second residual fraction thus obtained typically comprises compounds boiling above a temperature of 440°C. Preferably, the boiling point at which 10wt.% of the second residual fraction from step (d) is recovered is in the range between 440 and 560°C according to ASTM D7169, more preferably the boiling point at which 5 wt.% is recovered is in the range between 440 and 560°C according to ASTM D7169.

**[0035]** The second residual fraction is also known as a vacuum bottoms product. The second residual fraction may undergo a subsequent dewaxing step to obtain extra heavy base oil with a better pour point. With the term extra heavy base oil is meant a residual base oil.

50 [0036] In one embodiment, in which in step (b) a catalytic dewaxing catalyst is used, the second residual fraction is a residual base oil.

[0037] In another embodiment, in which in step (b) a hydroprocessing catalyst or a stacked bed of catalysts is used, the second residual fraction is further dewaxed to obtain a residual base oil.

**[0038]** Suitably, the residual base oil has a pour point below -5°, preferably in a range between -10°C and -40°C. Also, the residual base oil has a kinematic viscosity at 100°C in a range between 10 and 35 cSt, preferably between 12 and 30 cSt.

[0039] In a preferred embodiment, at least part of the second residual fraction is recycled to step (a).

[0040] In case of recycling of the second residual fraction or another fraction obtained in fractionation of the hydro-

processed feedstock, reference herein to the feedstock to step (a) is to the combined feedstock i.e. to the total of fresh feedstock and any recycled fraction.

**[0041]** The distillate base oil fraction as obtained in step (d) will have an intermediate boiling range. Preferably, the boiling point at which 90wt.% of the distillate base oil fraction from step (c) is recovered is in the range of from 420 and 560°C according to ASTM D2887.

**[0042]** In one embodiment, the process according to the present invention comprises a further step (e) wherein the distillate base oil fraction is fractionated in one or more base oils.

**[0043]** Although the catalyst activity is affected by the presence of the nitrogen containing compounds in step (b) of the process according to the present invention and hence the catalytic reaction takes place at a higher operating temperature, no negative impact on the yield profile is observed but surprisingly higher yields in distillate base oils and therefore also base oils are obtained.

**[0044]** In one embodiment, wherein in step (b) a hydroprocessing catalyst or a stacked bed of catalysts is used, the distillate base oil fraction obtained in step (d) may not be sufficiently isomerized. Preferably, the distillate base oil fraction of step (d) is catalytically dewaxed to obtain one or more base oils.

This distillate base oil fraction is also known as a waxy raffinate fraction. This waxy raffinate fraction may be further dewaxed and fractionated in one or more base oils and optionally an isomerized gasoil fraction, preferably in a base oil having a kinematic viscosity according to ASTM D445 at 100°C in a range of from 1.2 to 3 Cst and/or a base oil having a kinematic viscosity at 100°C in a range of from 3 to 5 Cst and/or in a base oil having a kinematic viscosity at 100°C in a range of from 5 to 7 and/or in a base oil having a kinematic viscosity according to ASTM D445 at 100°C in a range of from 7 to 9 Cst.

**[0045]** The yield of waxy raffinate fraction as obtained in step d) according to the process of the present invention increases upon increasing amount of nitrogen containing compound. In addition, the pour point of the waxy raffinate deceases upon the addition of an increasing amount of nitrogen compound. Both effects are surprising because the catalyst is affected by the presence of a nitrogen containing compound which results in performing the catalytic reaction in step (b) at higher temperature compared to a reaction without the presence of a nitrogen containing compound.

**[0046]** In another embodiment, in which in step (b) a catalytic dewaxing catalyst is used, the distillate base oil fraction obtained in step (d) is sufficiently isomerized and may be separated in one or more base oils and optionally an isomerized gasoil fraction. The distillate base oil fraction is separated in various base oils with a kinematic viscosity at 100°C in a range of from 1.2 to 9Cst.

<sup>30</sup> **[0047]** The following examples of certain aspects of some embodiments are given to facilitate a better understanding of the present invention. In no way should these examples be read to limit, or define, the scope of the invention.

EXAMPLE 1 (Comparative example)

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[0048] A noble metal containing hydrocracking catalyst consisting of 0.8 wt% platinum on a carrier containing 70 wt% silica-alumina and 30% binder was mixed in a 1:2 v/v ratio with silicon carbide and loaded into the reactor. The catalyst was reduced in hydrogen at 400 °C for two hours and tested with a Fischer-Tropsch feedstock comprising 81% of compounds boiling above 370 °C and 49% of compounds boiling above 540 °C. The N content as measured with modified ASTM D5762 was below detection limit of <0.5 ppmw. A total pressure of 60 bar was applied. Hydrogen with a purity of > 99% was added with a gas-hourly-space-velocity of 1250 NI/Icatalyst/h. The fresh liquid feed weight-hourly-space-velocity was 0.8 kg/lcatalyst/h.

[0049] The reaction products were separated with an atmospheric and vacuum distillation into a gaseous stream (C1-175°C), a liquid fraction (middle distillates (175-370°C), an intermediate liquid fraction (waxy raffinate fraction) and a heavy liquid fraction. The heavy liquid fraction was fully recycled to the inlet of the reactor. The recycle rate was chosen such that no accumulation of the heavy fraction in the system took place. Each fraction was analysed separately. The gaseous fraction was analysed with an online GC, the liquid fractions were collected over 24 hour periods and analysed by ASTM D 2887 (light fraction), ASTM D-2887 for the intermediate liquid fraction, whereas ASTM D7169-05 was used for the heavy fraction. The total product yield was calculated on the compositional data obtained for each stream and the quantity of hydrocarbon product in each stream. The conversion level was determined using atmospheric boiling point distributions for liquid feed and hydrocarbon products. The conversion 540°C+ material in the feed was varied by changing the Weight Average Bed Temperature over the reactor. The yield of the different product fractions was calculated on the basis of the generated data. In the comparative example the Fischer-Tropsch feedstock was used as is. In Table 1 the results obtained in above experiment at ~70% conversion of 540°C+ material is given.

55 Example 2 (according to the invention)

**[0050]** The feedstock of the experiment in example 1 was supplemented with 22.4 ppmw decylamine, equivalent to 2 ppmw N. In Table 1 the results obtained at  $\sim$ 70% of 540°C+ material is given and compared to the comparative example.

**[0051]** The results show that due to the addition of decylamine the activity of the catalyst decreased. The operating temperature was increased with 14 °C from 335 to 349°C to arrive at the same conversion of 540°C+ material. The yields to undesired light products decreased from 22.6 to 19.3 wt%. Middle distillate production was unchanged and the yield to waxy raffinate increased from 21.5 to 24.8 wt%. This demonstrates that the yield of the intermediate fraction or waxy raffinate, can be maximized by the addition of amines to the feedstock of an HPC unit.

Table 1

Decylamine	ppmw N	0	2
WABT		335	349
540 °C <sup>+</sup> conversion	woff%	71	70
Lights yield (C <sub>1</sub> -175 °C) C1	woff%	22.6	19.3
Middle distillate yield (175-370 °C)	woff%	56.1	56.1
Waxy Raffinate yield (370-540 °C)	woff%	21.5	24.8
Total	woff%	100.6	100.6

Example 3 (according to the invention)

**[0052]** In another experiment the feedstock to the HPC reactor was varied from 0 to 56 ppmw decylamine (0-5 ppmw N) and operated at constant conversion per pass. In Table 2 the measured pour point of the waxy raffinate are provided. The results indicate an improved (lower) pour point when amines are added to the feed. The gasoil cloud point slightly improved as well.

Table 2

Decylamine	ppmw N	0	1	2	5
Waxy Raffinate pour point	Deg C	24	15	18	15
Gasoil Cloud Point	Deg C	-19	-19	-22	-21

EXAMPLE 4 (according to the invention)

[0053] A noble metal containing hydrocracking catalyst consisting of 0.8 wt% platinum on a carrier containing 66 wt% silica-alumina, 4% zeolite beta and 30% binder was mixed in a 1:2 v/v ratio with silicon carbide and loaded into the reactor. The catalyst was reduced in hydrogen at 400 °C for two hours and tested with two different Fischer-Tropsch feedstocks. The first feedstock comprised 90% of compounds boiling above 370 °C did contain no (<0.5 ppmw N), whereas the second feedstock comprised 87% of compounds boiling above 370 °C and contained 3 ppmw N, present as a range of amines. A total pressure of 38 bar was applied. Hydrogen with a purity of > 99% was added with a gashourly-space-velocity of 1000 Nl/lcatalyst/h . The fresh liquid feed weight-hourly-space-velocity was 1.0 kg/lcatalyst/h. The reaction products were separated into a gaseous stream, a liquid and a heavy liquid fraction. The reaction was run in once-through mode and each fraction was analysed separately. The gaseous fraction was analysed with an online GC, the liquid fractions were collected over 24-hour periods and analysed by ASTM D 2887 (light fraction) whereas ASTM D7169-05 was used for the heavy fraction. The total product yield was calculated on the compositional data obtained for each stream and the quantity of hydrocarbon product in each stream. The conversion level was determined using atmospheric boiling point distributions for liquid feed and hydrocarbon products. The conversion 370°C+ material in the feed was varied by changing the Weight Average Bed Temperature over the reactor. The yield of the different product fractions was calculated on the basis of the generated data.

**[0054]** The results provided in Table 4 indicate a significantly improved selectivity: lower fraction of light products and increased middle distillate and waxy raffinate yield are found when amines are present in the feedstock.

Table 3

Amines	ppmw N	0	3
WABT		306	319
370 °C+ conversion	woff%	49	49

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(continued)

Amines	ppmw N	0	3
Lights yield (C <sub>1</sub> -175 °C)	woff%	13.7	11.7
Middle distillate yield (175-370 °C)	woff%	40.6	44.0
Waxy Raffinate yield (370-540 °C)	woff%	25.3	27.4
Heavies yield (>540 °C)	woff%	20.4	16.8

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#### Claims

1. Process to prepare at least middle distillates and base oils from a Fischer-Tropsch derived feedstock, by

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(a) providing a Fischer-Tropsch derived feedstock containing nitrogen through addition of a nitrogen containing compound selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring to a Fischer-Tropsch reactor;

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(b) subjecting the feedstock of step (a) to a hydroprocessing step in the presence of one or more catalysts to obtain a first mixture comprising one or more middle distillate fractions and a first residual fraction and naphtha

(c) separating the first mixture as obtained in step (b) by means of atmospheric distillation into one or more middle distillate fractions, a first residual fraction and a naphtha fraction;

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(d) separating the first residual fraction by means of vacuum distillation into at least a distillate base oil fraction and a second residual fraction.

2. Process according to claim 1, wherein the provided Fischer-Tropsch feedstock of step (a) is prepared by adding to a Fischer-Tropsch product stream as obtained from a Fischer-Tropsch process a nitrogen containing compound selected from ammonia, HCN, NO, amines, nitriles and a heterocyclic compound containing at least one nitrogen atom as ring member of a heterocyclic ring.

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3. Process according to claim 1 or 2, wherein the nitrogen containing compound is present in the Fischer-Tropsch feedstock of step (a) in a concentration between 0.5 and 10 ppmw.

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4. Process according to any of the preceding claims, wherein the nitrogen containing compound comprises amines.

5. Process according to claim 4, wherein the amine is decylamine.

dewaxed to obtain one or more base oils.

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6. Process according to any one of the preceding claims, wherein in the presence of one or more catalysts of step (b) both hydrocracking and hydroisomerization takes place.

7. Process according to any one of the preceding claims, wherein one or more catalyst of step (b) comprises a Group VIII noble metal supported on an amorphous acidic carrier.

9. Process according to any of the preceding claims, wherein the distillate base oil fraction of step (d) is catalytically

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8. Process according to any of the preceding claims, wherein one or more catalyst of step (b) comprises a Group VIII metal and a medium pore size molecular sieve.

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# **EUROPEAN SEARCH REPORT**

**Application Number** EP 20 20 8595

	DOCUMENTS CONSID				
Category	Citation of document with in of relevant passa			elevant claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	W0 2017/037176 A1 ( [NL]; SHELL OIL CO 9 March 2017 (2017- * page 19, line 3 - figure 1 * * page 17, line 32	[US]) 03-09) line 4; claims	1,2,3;	9	INV. C10G45/58 C10G47/00 C10G65/12
x	WO 2017/037177 A1 ( [NL]; SHELL OIL CO 9 March 2017 (2017- * page 15, lines 1- claims 1,13,14 *	[US]) 03-09)		9	
X	GB 2 394 721 A (CHE 5 May 2004 (2004-05 * claims 1,18,25,29 tables 2,3 *	-05)	-	9	
X	US 2004/256286 A1 ( ET AL) 23 December * paragraphs [0039] [0060]; claims 1,8;	2004 (2004-12-23 - [0044], [005	)	) - -	TECHNICAL FIELDS SEARCHED (IPC)
X,D	W0 2015/063213 A1 ( [NL]; SHELL OIL CO 7 May 2015 (2015-05 * page 6, line 25 - * page 10, line 1 - * page 13, line 8 - * page 14, line 7 -	[US]) -07) line 27; claims line 9 * line 25 *			
	The present search report has b	·			- Francisco
Place of search  The Hague		Date of completion o		Deur	rinck, Patricia
X : parti Y : parti docu A : tech	ATEGORY OF CITED DOCUMENTS  cularly relevant if taken alone cularly relevant if combined with anoth ment of the same category nological background	E : ea afte ner D : do L : doc		t, but publish pplication r reasons	ned on, or
	-written disclosure mediate document		mber of the same pa ument	uent ramily,	corresponding

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

EP 20 20 8595

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-04-2021

10	Patent document cited in search report		Publication date		Patent family member(s)	Publication date	
15	WO 2017037176	A1	09-03-2017	CN EP US WO ZA	107949624 A 3344729 A1 2018251683 A1 2017037176 A1 201801286 B	20-04-2018 11-07-2018 06-09-2018 09-03-2017 19-12-2018	
20	WO 2017037177	A1	09-03-2017	CN EP US WO ZA	107922852 A 3344730 A1 2018258354 A1 2017037177 A1 201801287 B	17-04-2018 11-07-2018 13-09-2018 09-03-2017 19-12-2018	
25	GB 2394721	A	05-05-2004	AU AU GB NL US WO ZA	2003247995 A1 2003277061 A1 2394721 A 1024648 C2 2004087824 A1 2004041772 A1 200307627 B	20-05-2004 07-06-2004 05-05-2004 18-05-2010 06-05-2004 21-05-2004 05-07-2004	
35	US 2004256286	A1	23-12-2004	AU BR CN GB JP JP NL US WO ZA	2004252511 A1 PI0411616 A 1836028 A 2418673 A 5481014 B2 2007520580 A 1026464 C2 2004256286 A1 2005001006 A2 200600303 B	06-01-2005 08-08-2006 20-09-2006 05-04-2006 23-04-2014 26-07-2007 09-08-2005 23-12-2004 06-01-2005 28-11-2007	
45	WO 2015063213	A1	07-05-2015	CN EA EP US WO ZA	105683339 A 201690901 A1 3063254 A1 2016251583 A1 2015063213 A1 201602702 B	15-06-2016 31-08-2016 07-09-2016 01-09-2016 07-05-2015 26-07-2017	
50							
<b>55</b> FORM P0459							

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#### REFERENCES CITED IN THE DESCRIPTION

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#### Patent documents cited in the description

- US 6635171 B2 [0002] [0003]
- WO 2003070857 A **[0012]**

- WO 2011064236 A [0025] [0029]
- WO 2015063213 A [0027] [0029]

# Non-patent literature cited in the description

 JULIUS SCHERZER; A. J. CRUIA. Hydrocracking Science and Technology. Marcel Dekker, Inc, 1996 [0022]