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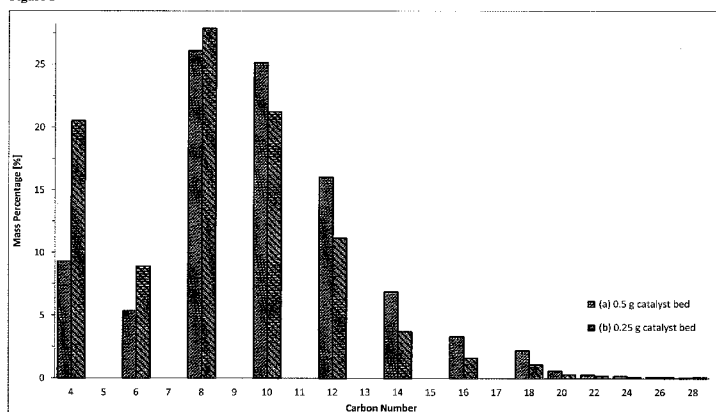
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(54) Title: PRODUCTION OF MIDDLE DISTILLATE HYDROCARBON COMPOSITION

Figure 1



(57) Abstract: A process for the preparation of a middle distillate hydrocarbon composition from ethylene, wherein said process comprises the following steps: (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara; (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range; (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process; (d) cracking the heavy product stream D in a cracking reactor to produce a cracked product stream E; (e) separating a middle distillate product F from the cracked product stream E; and (f) hydrogenating the middle distillate product stream C, wherein the middle distillate hydrocarbon composition comprises at least a portion of the hydrogenated middle distillate product stream C and at least a portion of the middle distillate product F.



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PRODUCTION OF MIDDLE DISTILLATE HYDROCARBON COMPOSITION

The present invention relates to the production of a middle distillate hydrocarbon composition from an ethylene composition, said process comprising the oligomerisation of ethylene. Also provided by the present invention is a process for the conversion of an ethanol composition into a middle distillate hydrocarbon composition, said process comprising the dehydrogenation of ethanol to ethylene and subsequent oligomerisation of the ethylene to a middle distillate hydrocarbon composition.

Diesel fuel, jet fuel and other middle distillate hydrocarbon compositions are typically derived from crude oil in oil refineries. There is an interest in alternative sources of, and/or alternative methods of preparing, middle distillate hydrocarbon compositions.

Hydrogenated vegetable oil may be used as an alternative for Diesel fuel; however, due to the oxygen content of the molecules within the hydrogenated vegetable oil, it is not approved for use as a jet fuel. Fischer-Tropsch processes are suitable for preparing middle distillate hydrocarbon compositions and the products of which are useful in all applications of middle distillate hydrocarbon compositions.

An alternative route for the preparation of Diesel fuel base stock is by the direct conversion of ethanol, such as described in US 2007/0287873 A1.

Another alternative route to middle distillate hydrocarbon compositions that has been proposed in the art is by the oligomerisation of ethylene. For example, WO 2011/138520 A2 discloses a method for producing medium-distilling hydrocarbon bases from a biomass-derived feedstock, said method including a step of purifying said feedstock, a step of dehydrating said purified feedstock into a predominantly ethylenic effluent including water, said step being carried out in the presence of an amorphous or zeolytic acid catalyst, at least one step of separating water and/or purifying, a first step of oligomerizing into at least one light olefinic effluent including at least 50 wt % of olefins having a number of carbon atoms greater than or equal to 4, in the presence of a catalyst including at least one Group VIII element and a porous refractory oxide substrate, a second step of oligomerizing; producing medium-distilling hydrocarbon bases in the presence of an amorphous or zeolytic catalyst having at least pore openings containing 10 or 12 oxygen atoms, and a step of fractionating the effluent from the oligomerization step.

WO 2010/066830 A1 discloses a process to make alpha olefins comprising:

dehydrating ethanol to recover an ethylene stream, introducing said ethylene stream into an oligomerization zone containing an oligomerization catalyst and into contact with said oligomerization catalyst, operating said oligomerization zone at conditions effective to produce an effluent consisting essentially of 1-butene, 1-hexene, optionally heavier alpha olefins and unconverted ethylene if any, introducing the above effluent into a fractionation zone to recover a stream consisting essentially of 1-butene, a stream consisting essentially of 1-hexene, optionally a stream consisting essentially of heavier alpha olefins and an optional ethylene stream. In another embodiment of WO 2010/066830 A1, the 1-hexene or at least one heavier alpha olefins, if any, are isomerized to an internal olefin and subsequently transformed by metathesis with the aid of additional ethylene into different alpha-olefins with even or odd number of carbons. By way of example, 1-hexene is isomerized into 2-hexene and by methathesis with ethylene converted to 1-pentene and propylene. In another embodiment of WO 2010/066830 A1, the oligomerization zone is only a dimerization zone and butene is produced. 1-butene is isomerized to 2-butene and sent to a methathesis zone in the presence of ethylene to be converted to propylene. In said embodiment the dehydration catalyst is selected in the group consisting of a crystalline silicate having a ratio Si/Al of at least about 100, a dealuminated crystalline silicate, and a phosphorus modified zeolite.

In "Catalysts and conditions for the highly efficient, selective and stable heterogeneous oligomerisation of ethylene", J. Heveling, C.P. Nicolaides, M.S. Scurrall, Applied Catalysis A: General 173 (1998), 1-9, the oligomerisation of ethylene using a heterogeneous nickel catalyst is disclosed for the preparation of products in the C₄-C₂₀ range and present a characterization of a straight-run diesel product obtained from ethylene.

There remains a need in the art for processes which are effective for the production of middle distillate hydrocarbon compositions.

In a first aspect, the present invention provides a process for the preparation of a middle distillate hydrocarbon composition from ethylene, wherein said process comprises the following steps:

- (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of

from 30 to 300 °C and a pressure of at least 10 bara;

- 5 (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range, the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range;
- 10 (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
- (d) cracking the heavy product stream D in a cracking reactor to produce a cracked product stream E;
- (e) separating a middle distillate product F from the cracked product stream E; and
- 15 (f) hydrogenating the middle distillate product stream C,

wherein the middle distillate hydrocarbon composition comprises at least a portion of the hydrogenated middle distillate product stream C and at least a portion of the middle distillate product F.

20 In one particular embodiment of the present invention, the ethylene composition may be derived from the dehydration of ethanol.

Thus, in another aspect of the present invention, there is provided a process for the preparation of a middle distillate hydrocarbon composition from ethanol, wherein said process comprises the following steps:

- 25 (1) feeding an ethanol composition to a dehydration reactor containing an ethanol dehydration catalyst, wherein the dehydration reactor is operated at a temperature and pressure effective to dehydrate at least part of the ethanol to ethylene and water;
- (2) separating a stream comprising ethylene from the effluent of the dehydration reactor of step (1);
- 30 (3) subjecting the stream comprising ethylene from step (2) to a process for removing any water, alcohols or other oxygenates which may be present to form an ethylene composition; and

(4) preparing the middle distillate hydrocarbon composition from the ethylene composition from step (3) in accordance with the process for the preparation of a middle distillate hydrocarbon composition as described herein.

In yet a further embodiment of the present invention, the middle distillate hydrocarbon composition is suitable for use as a Diesel fuel or is suitable for use as a component in a Diesel fuel. Thus, the present invention also provides a Diesel fuel composition comprising a Diesel fuel base stock and a middle distillate hydrocarbon composition prepared according a process as described herein.

In yet a further embodiment of the present invention, the middle distillate hydrocarbon composition is suitable for use as a jet fuel or is suitable for use as a component in a jet fuel. Thus, the present invention also provides a jet fuel composition comprising a jet fuel base stock and a middle distillate hydrocarbon composition prepared according a process as described herein.

In yet a further embodiment of the present invention, the middle distillate hydrocarbon composition is suitable for use as a marine or static engine fuel or is suitable for use as a component in a marine or static engine fuel. Thus, the present invention also provides a marine or static engine fuel composition comprising a marine or static engine fuel base stock and a middle distillate hydrocarbon composition prepared according a process as described herein.

In yet a further embodiment of the present invention, the middle distillate hydrocarbon composition is suitable for use as a fuel for a turbine engine or is suitable for use as a component in a fuel for a turbine engine. Thus, the present invention also provides a turbine fuel composition comprising a turbine fuel base stock and a middle distillate hydrocarbon composition prepared according a process as described herein.

In yet a further embodiment of the present invention, the middle distillate hydrocarbon composition is suitable for use as a heating fuel or is suitable for use as a component in a heating fuel. Thus, the present invention also provides a heating fuel composition comprising a heating fuel base stock and a middle distillate hydrocarbon composition prepared according a process as described herein.

In yet a further embodiment of the present invention, the middle distillate hydrocarbon composition is suitable for use as a lamp oil or is suitable for use as a component in a lamp oil. Thus, the present invention also provides a lamp oil composition

comprising a lamp oil base stock and a middle distillate hydrocarbon composition prepared according a process as described herein.

In the process of the present invention, an ethylene composition is fed to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operating at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara.

By the term “supported nickel oligomerisation catalyst”, it is meant a solid catalyst comprising nickel and at least one catalyst support, wherein the method of forming the catalyst is not limited and may include any method which results in a solid catalyst comprising a solid catalyst support and nickel.

The supported nickel oligomerisation catalyst contained within the oligomerisation reaction zone can be any supported nickel catalyst which is capable of oligomerising ethylene composition under at a temperature in the range of from 30 to 300 °C and at a pressure of at least 10 bara.

Preferably, the support for the oligomerisation catalyst comprises at least one porous material comprising silicon, aluminium and oxygen; examples of suitable porous material comprising silicon, aluminium and oxygen include amorphous silica-alumina and zeolites. More preferably, the support for the oligomerisation catalyst is based on at least one material selected from amorphous silica-alumina, zeolites or mixtures thereof.

In one particular embodiment, the support for the oligomerisation catalyst is selected from amorphous silica-alumina or a zeolite, with amorphous silica-alumina being preferred.

The supported nickel oligomerisation catalyst may be formed by any means of preparation of such catalysts known in the art. Examples suitable methods of preparing the supported nickel oligomerisation catalyst include impregnation, ion exchange and coprecipitation.

In one embodiment, the supported nickel oligomerisation catalyst is formed by impregnation of a nickel compound on a support, followed by drying and calcination of the impregnated support. The drying and calcination of the impregnated support may occur in a single step or as two or more separate steps. Typically, the nickel compound used for the preparation of the supported nickel oligomerisation catalyst by impregnation will be a soluble nickel salt.

In another embodiment, the supported nickel oligomerisation catalyst is formed by ion exchange of a nickel ion on to a support, followed by drying and calcining the ion-exchanged support. The drying and calcination of the ion-exchanged support may occur simultaneously or as two or more separate steps. The support used for the preparation of the supported nickel oligomerisation catalyst by ion-exchange will contain suitable sites which are capable of being ion-exchanged with a nickel ion. Suitable examples include zeolites and amorphous silica-alumina, in particular in either the acidic form or in the ammonium form.

In a further embodiment, the supported nickel oligomerisation catalyst can be prepared by coprecipitated of the nickel with the support material, such as described in, for example, US 5,849,972, the contents of which are incorporated herein by reference. The composition formed by coprecipitation will be dried and calcined prior to use as a supported nickel oligomerisation catalyst. The drying and calcination of the composition formed by coprecipitation may occur as a single step or as two or more separate steps.

Methods of impregnation, ion-exchange and coprecipitation would be known to a person skilled in the art.

The type of nickel compound used in the formation of the supported nickel oligomerisation catalyst is not limited, provided that it is suitable for use in the method of preparation employed. Typically, the nickel will be a soluble nickel salt or nickel complex. Examples of suitable nickel compounds which may be used in the preparation of the supported nickel oligomerisation catalyst include the nickel nitrate salts, nickel sulphate salts, nickel acetate salts, and mixtures thereof.

In one particular embodiment, the supported nickel oligomerisation catalyst comprises at least 0.1 wt% nickel, based upon the weight of the dry catalyst, preferably at least 0.2 wt% nickel, more preferably at least 0.3 wt% nickel, even more preferably at least 0.4 wt% nickel; in this embodiment, the supported nickel oligomerisation catalyst also comprises at most 50 wt% nickel, based upon the weight of the dried catalyst, preferably at most 40 wt% nickel, more preferably at most 30 wt% nickel, even more preferably at most 20 wt% nickel. Specific examples according to this embodiment include supported nickel oligomerisation catalysts comprising from 0.1 to 50 wt% nickel, 0.1 to 50 wt% nickel, 0.2 to 50 wt% nickel, 0.3 to 50 wt% nickel, 0.4 to 50 wt% nickel, 0.1 to 40 wt% nickel, 0.2 to 40 wt% nickel, 0.3 to 40 wt% nickel, 0.4 to 40 wt% nickel, 0.1 to 30 wt% nickel, 0.2 to

30 wt% nickel, 0.3 to 30 wt% nickel, 0.4 to 30 wt% nickel, 0.1 to 20 wt% nickel, 0.2 to 20 wt% nickel, 0.3 to 20 wt% nickel and 0.4 to 20 wt% nickel, based upon the total weight of the dry catalyst.

In the embodiments wherein the catalyst is formed by impregnation or by ion
5 exchange, the supported nickel oligomerisation catalyst preferably comprises from 0.1 to 10 wt% nickel, based upon the weight of the dried catalyst, preferably at least 0.2 to 8 wt% nickel, more preferably at least 0.3 to 6 wt% nickel.

In the embodiments wherein the catalyst is formed by coprecipitation, the supported
10 nickel oligomerisation catalyst preferably comprises from 0.1 to 50 wt% nickel, based upon the weight of the dried catalyst, preferably from 0.2 to 40 wt% nickel, more preferably at least 0.3 to 30 wt% nickel, even more preferably from 0.4 to 20 wt% nickel.

In the embodiment wherein the nickel is impregnated on to the support, it is typically
impregnated on to the support in the form of soluble nickel compound, such as a salt or
complex. Suitable nickel compounds and solvents will be known to one skilled in the art.
15 Examples of suitable nickel compounds include nickel nitrates, nickel acetates, nickel sulphates, nickel sulphonates, nickel phosphates, nickel phosphonates, nickel chloride, nickel bromide, nickel carbonate, nickel perchlorates, and mixtures thereof.. Examples of suitable solvents include water, methanol, ethanol, dimethyl ether, diethyl ether, and mixtures thereof; preferably, the solvent is selected from water, ethanol and mixtures
20 thereof, more preferably water. The impregnated support is then washed, dried and calcined to form the supported nickel oligomerisation catalyst.

In the embodiment wherein the nickel is ion exchanged on to the support, the nickel
is in the form of soluble cationic nickel compound, such as a nickel salt or cationic nickel
complex, wherein a solution containing the cationic nickel compound is refluxed with the
25 support for sufficient time such that at least a portion of the cationic sites on the support have been ion exchanged with the nickel cation. Examples of suitable nickel compounds include nickel nitrates, nickel acetates, nickel sulphates, nickel sulphonates, nickel phosphates, nickel phosphonates, nickel chloride, nickel bromide, nickel carbonate, nickel perchlorates, and mixtures thereof.. Examples of suitable solvents include water,
30 methanol, ethanol, dimethyl ether, diethyl ether, and mixtures thereof; preferably, the solvent is selected from water, ethanol and mixtures thereof, more preferably water. The ion-exchanged support is then washed, dried and calcined to form the supported nickel

oligomerisation catalyst.

In the embodiment wherein the supported nickel oligomerisation catalyst is prepared by coprecipitation, it is prepared by any suitable coprecipitation method known to one skilled in the art. In one example of this embodiment, the nickel is in the form of soluble nickel salt, wherein a solution of the nickel salt is admixed with a solution of the soluble aluminium compound, such as a salt, to form a solution comprising dissolved nickel and aluminium salts; the solution comprising dissolved nickel and aluminium salts is then admixed with an alkali metal waterglass solution, such as a sodium waterglass, at essentially constant pH and mixing. The desired coprecipitated composition forms a solid suspension in the solution, which is then filtered and washed until it is free of salts. Examples of suitable nickel salts include nickel nitrates, nickel acetates and nickel sulphates; examples of suitable aluminium salts include aluminium nitrates, aluminium acetates and aluminium sulphates. Typically the solvent used is water. The catalyst formed by coprecipitation is then washed, dried and calcined to form the supported nickel oligomerisation catalyst.

If the supported nickel oligomerisation catalyst prepared is not in the form of shaped particles, it may be formed into shaped particles, optionally with a binder, prior to use, for example by pelletisation or extrusion. If the catalyst is formed into shaped particles, then the shaped particles are typically dried and calcined prior to use in the oligomerisation process of the present invention. Alternatively, the supported nickel oligomerisation catalyst may be used in the form of a powder.

The oligomerisation reaction zone comprises at least one oligomerisation reactor. In one particular embodiment, the oligomerisation reaction zone comprises one oligomerisation reactor. In another particular embodiment, the oligomerisation zone comprises two or more reactors, said reactors being connected either in series, in parallel, or in combinations thereof.

The type of reactor used in the oligomerisation reaction zone is not limited. Suitable types of reactors which may be used in the oligomerisation reaction zone of the present invention include fixed bed reactors, slurry bed reactors and bubble column reactors.

The oligomerisation reaction of step (a) is operated at a temperature in the range of from 50 to 300 °C, preferably at a temperature in the range of from 50 to 250 °C and more preferably a temperature in the range of from 100 to 200 °C.

The oligomerisation reaction of step (a) is operated at a pressure of at least 10 bara,

preferably at a pressure in the range of from 10 to 100 bara and more preferably a pressure in the range of from 30 to 70 bara, such as, for example, in the range of from 50 to 70 bara.

The rate, in terms of mass hourly space velocity (MHSV), calculated as kg ethylene per kg dry catalyst per hour, at which the ethylene composition is fed to the
5 oligomerisation reaction zone is preferably in the range of from 0.01 to 20 h⁻¹, more preferably from 0.05 to 15 h⁻¹, even more preferably from 0.1 to 10 h⁻¹.

The ethylene composition which is fed to the oligomerisation reaction zone comprises ethylene and may optionally contain other components which do not act as a catalyst poison or otherwise interfere with the supported nickel oligomerisation catalyst,
10 such as diluents and/or solvents. Suitable diluents which may be included include nitrogen and other inert gases, such as the noble gases and gaseous alkanes. Suitable solvents which may be used include inert hydrocarbons, such as alkanes and naphthenes. In the embodiment where a solvent is used, the solvent may be an alkane or naphthene which boils within the boiling point range of the light products stream B and thus gets recycled
15 back to the oligomerisation reaction zone in step (c) of the process; alternatively, the solvent may be an alkane or naphthene which boils above the boiling point range of the light products stream B and forms part of the middle distillate product stream C. One particularly suitable solvent which may be used in this embodiment of the present invention is at least of portion of the middle distillate hydrocarbon composition prepared
20 by the process of the present invention.

Depending upon the source of the ethylene composition, the ethylene composition which is fed to the oligomerisation reaction zone may also optionally contain other olefinic components. In one embodiment, the amount of olefins having three or more carbon atoms present in the ethylene composition which is fed to the oligomerisation reaction zone is at
25 most 20 mol%, preferably at most 15 mol%, more preferably at most 10 mol%.

The water content of the total feed to the oligomerisation reaction zone is typically kept as low as possible; wherein the total feed to the oligomerisation reaction zone is the total amount of all feed streams, e.g. ethylene composition and recycled streams that are fed to oligomerisation reaction zone. Preferably, the water content of the total feed to the
30 oligomerisation reaction zone is at most 0.1 wt%, more preferably it is at most 0.01 wt% and even more preferably at most 0.001 wt%, for example having no detectable water content.

The source of the ethylene composition used in the process of the present invention is not limited and any available source of ethylene may be used.

In one embodiment the ethylene composition is derived from a hydrocarbon source, for example by pyrolysis of hydrocarbons, such as natural gas or naphtha, or by steam
5 cracking of hydrocarbons, such as naphtha.

In another embodiment of the present invention, the ethylene composition may be derived from a "methanol to olefin" process, wherein methanol or dimethyl ether is subjected to a dehydration process to produce an olefinic product composition.

In another embodiment of the present invention, the ethylene composition may be
10 derived from the dehydration of ethanol. In this embodiment, the ethanol may be derived from any known synthetic source or it may be a bioethanol. In the embodiment of the present invention wherein the ethylene composition is derived from the dehydration of bioethanol, the process of the present invention may be used to prepare a biomass derived middle distillate hydrocarbon composition which may be used in fuels, in particular in
15 Diesel fuels or in jet fuels.

Thus, in one particular aspect of the present invention, the ethylene composition used in the preparation of the middle distillate hydrocarbon composition is derived from ethanol by a process which comprises the following steps:

- (1) feeding an ethanol composition to a dehydration reactor containing an ethanol
20 dehydration catalyst, wherein the dehydration reactor is operated at a temperature and pressure effective to dehydrate at least part of the ethanol to ethylene and water;
- (2) separating a stream comprising ethylene from the effluent of the dehydration reactor of step (1);
- 25 (3) subjecting the stream comprising ethylene from step (2) to a process for removing any water, alcohols or other oxygenates which may be present to form an ethylene composition;

wherein the ethylene composition stream of step (3) is used as the source of ethylene composition in the preparation of a middle distillate hydrocarbon composition in
30 accordance with the first aspect of the invention as described herein.

In the embodiment wherein the ethylene composition is produced by the dehydration of bioethanol, the bioethanol is produced from a biological source, for example by

fermentation of biomass and/or a derivative thereof. The term "biomass" as used herein refers to any biological source of a carbohydrate which may be converted to ethanol by fermentation of the biomass directly or fermentation of a derivative of the biomass; for example biological sources of sugars, starches and cellulose. For instance, bioethanol may
5 be obtained by fermentation of feedstocks derived from sugar cane, such as sugar cane molasses and sugar cane juice; sugar beet, such as sugar beet molasses and sugar beet juice; cereal crops, such as corn or wheat derived feedstocks like corn syrup; and lignocellulosic materials, such as fast growing grasses or "energy grasses".

Alternatively, the ethanol may be derived from a fermentation process performed on
10 a feed stream comprising carbon monoxide and hydrogen, such as synthesis gas. Such processes are described in, for example, WO 2012/062633 A1; the fermentation process described therein being incorporated herein by reference.

In the embodiment wherein the ethylene composition which is fed to the oligomerisation reaction zone is derived from the dehydration of ethanol, the ethanol
15 composition which is fed to the dehydration reactor contains at least 50 wt% ethanol, more preferably at least 70 wt% ethanol, even more preferably at least 80 wt% ethanol, for example at least 90 wt%, provided that such other compounds would not adversely affect the dehydration catalyst or otherwise negatively impact on the dehydration process by, for example, reacting with the ethylene produced under the dehydration conditions or reacting
20 with the ethanol under the dehydration conditions. In one particular embodiment, the ethanol composition is a hydrous ethanol composition. Such hydrous ethanol compositions may be the raw or crude ethanol composition which is resultant from the distillation of an ethanol product which has been obtained by the fermentation of biomass without further subjecting the obtained ethanol to a dewatering step. Such hydrous ethanol compositions
25 may contain an amount of water which is equal to or greater than the amount of water which is determined by the azeotrope of the ethanol water composition produced during the fermentation process. Preferably, the ethanol composition which is fed to the dehydration reactor comprises less than 5 wt% of compounds other than ethanol, diethyl ether or water, preferably less than 2 wt% of compounds other than ethanol, diethyl ether
30 or water, more preferably less than 1 wt% of compounds other than ethanol, diethyl ether or water.

Depending upon the source of ethanol, it may be desirable to subjecting to a

purification step prior to feeding to the dehydration reactor; in particular, it has been observed that certain impurities which may be present in bioethanol, such as certain cationic, anionic, acidic, basic or nitrogenous impurities may negatively impact on the performance and/or life of the dehydration catalyst. Therefore, in one particular
5 embodiment, the ethanol composition is subjected to a purification stage prior to being fed to the dehydration reactor, where the ethanol composition is a bioethanol composition; it is preferable that said bioethanol composition is first subjected to a purification stage prior to being fed to the dehydration reactor.

10 Examples of impurities which it may be desirable to remove from the ethanol composition prior to feeding to the dehydration reactor include nitrogen-containing contaminants, such as nitriles, amines, ammonium cations, amides, imides and heterocyclic nitrogen-containing compounds, aldehydes, ketones, carboxylic acids, carboxylic esters, and thio-compounds.

15 Thus, in one embodiment wherein the ethylene composition which is fed to the oligomerisation reaction zone is derived from the dehydration of ethanol, the ethanol composition is subjected to a purification stage in order to reduce the amount of impurities which are present in the ethanol composition. The purification stage may be implemented by means that are known to one skilled in the art, such as, for example, the use of at least one resin, the adsorption of impurities in/on a solid that is selected from among the
20 molecular sieves, active carbon, alumina, aluminosilicates including zeolites, silica-aluminas and silicates, and distillation. Depending upon the nature of the impurities present, a further pretreatment stage may also be employed, such as a hydrogenation stage performed on the ethanol composition to hydrogenate any multiple bonds between carbon atoms and carbon atoms and any heteroatoms which may be present in any compounds in
25 the ethanol composition, in the presence of a nickel-based catalyst, whereby said pretreatment stage is carried out before or after said purification stage.

The ethanol dehydration catalyst in the dehydration reactor of step (1) may be any of the ethanol dehydration catalysts that are known in the art. For example, the ethanol dehydration catalyst may be a crystalline silicate, a dealuminated crystalline silicate or a
30 phosphorus modified zeolite as described in WO 2009/098262, the contents of which are incorporated herein by reference. Alternatively, the ethanol dehydration catalyst may be a heteropolyacid catalyst, for instance as described by WO 2008/138775 and

WO 2008/062157, the contents of which are incorporated herein by reference. In preferred embodiments, the ethanol dehydration catalyst is a heteropolyacid catalyst. The heteropolyacid catalyst is preferably supported on a suitable inert support, such as silica or alumina.

5 Suitable conditions for dehydrating alcohols are known in the art and would be known to the skilled person, for instance with reference to the prior art documents cited herein. However, in the case of a crystalline silicate or zeolite alcohol dehydration catalyst, typical reaction conditions include a temperature of from 280 to 500 °C, a total pressure of from 0.5 to 30 bara, and a partial pressure of ethanol that is preferably from 1.2
10 to 4 bara. In the case of a heteropolyacid catalyst, typical reaction conditions include a temperature of from 180 to 270 °C and a pressure of from 1 to 45 bara.

 Preferably, the ethanol composition is fed to the dehydration reactor in the vapour phase.

 The effluent from the dehydration reactor comprises at least ethylene and water, and
15 may also comprise unreacted ethanol and diethyl ether by-product, both of which may conveniently be recycled back to the dehydration reactor.

 The separation of an ethylene stream from the dehydration reactor effluent may be achieved by any means known in the art, such as flash separation.

 Prior to feeding the ethylene produced by the dehydration of ethanol stream to the
20 oligomerisation reaction zone, it may be desirable to subject the ethylene stream to a process for removing any water, alcohols or other oxygenates which may be present therein; by the term other oxygenates used herein, it is meant any compound in the effluent which contains at least one oxygen atom, such as, for instance, diethyl ether, acetaldehyde, ethyl acetate, carbon monoxide and carbon dioxide. The removal of any water, alcohols or
25 other oxygenates which may be present may conveniently be achieved by any process or combination of processes known in the art.

 In one embodiment, the process for removing any water, alcohols or other oxygenates which may be present is achieved by passing the ethylene stream through a suitable guard bed or guard beds. Molecular sieve 3A is a well-known material which is
30 suitable for use in removing water from an ethylene stream and may be used as a guard bed to remove at least water from an ethylene stream.

 In another embodiment, the process for removing any water, alcohols or other

oxygenates which may be present is achieved by one or more distillation processes.

In another embodiment, the ethylene composition may comprise a mixture of ethylene which has been derived from two or more sources; such as a mixture of ethylene which has been derived from the cracking of a hydrocarbon source and ethylene which has been derived from the dehydration of ethanol.

The oligomerisation product A formed in the oligomerisation reaction zone of step (a) consists of any unreacted ethylene, any diluents or solvents fed to or present in the oligomerisation reaction zone, and products of the oligomerisation reaction. The products of the oligomerisation reaction comprises a mixture of straight and branched chain olefins, wherein said olefins comprise a mixture of both alpha-olefins and internal olefins, with the majority of the oligomerisation products having an even number of carbon atoms. The distribution of carbon numbers in the oligomerisation products will be dependent upon the nature and amount of light products stream B that is recycled to the oligomerisation reaction zone. In one embodiment, the proportion of internal olefins in the oligomerisation products increase with increasing carbon chain length and/or the proportion of branched compounds in the oligomerisation products increase with increasing carbon chain length. In one embodiment, the fraction of the oligomerisation products which boils above the light products stream B comprises greater than 50 mol% internal olefins.

In step (b) of the process, a light products stream B, a middle distillate product stream C and a heavy products stream D are separated from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range, the middle distillate product stream C consists of a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range. By the term "mono-olefin boiling range" it is meant the boiling points of the olefin compositions having the empirical formula C_xH_{2x} , for example the C8 mono-olefin boiling range is the boiling range of olefins having the empirical formula C_8H_{16} .

In one embodiment, the light products stream B consists of the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range. However, if the middle distillate product which is desired has an initial boiling point which is higher

than the boiling point of the C8 mono-olefins in the oligomerisation product A, then the light products stream B may consist of the fraction of oligomerisation product A which boils below the lowest boiling point of the middle distillate product stream C.

Any components in the oligomerisation product A which may be present and have a boiling point below the boiling point of ethylene (-103.7 °C at atmospheric pressure (1.013 bar)) may also be included in the light products fraction. To prevent build-up of any components having a boiling point below the boiling point of ethylene or any inert compounds, such as alkanes, in the oligomerisation process, part of light products stream B may be purged during the step of recycling at least part of the light products stream B.

In one embodiment of the present invention, the light products stream B boils below 130 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 130 °C, in particular in the range of from -103.7 °C to 130 °C, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below 140 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 140 °C, in particular in the range of from -103.7 °C to 140 °C, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below 150 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 150 °C, in particular in the range of from -103.7 °C to 150 °C, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below 160 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 160 °C, in particular in the range of from -103.7 °C to 160 °C, at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils below 170 °C at atmospheric pressure (at 1.013 bar). In another embodiment of the present invention, the light products stream B boils in the range of from -105 °C to 170 °C, in particular in the range of from -103.7 °C to 170 °C, at atmospheric pressure (at 1.013 bar).

The middle distillate product stream C will comprise of at least part of the fraction of oligomerisation product A that boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D. In one particular embodiment

of the present invention, the middle distillate product stream C will comprise the entire fraction of oligomerisation product A that boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D.

The heavy products stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range. The lower boiling point limit of the heavy products stream D may conveniently be determined by the desired upper boiling point of the middle distillate product stream C; thus, depending upon the desired composition of the middle distillate hydrocarbon composition, the heavy products stream D may consist of the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range, alternatively, the heavy products stream D may consist of the fraction of oligomerisation product A which boils above a temperature selected from 350 °C, 330 °C, 320 °C, 310 °C, 290 °C, 280 °C, 270 °C, 260 °C and 250 °C. In another particular embodiment, the heavy product stream D comprises the fraction of oligomerisation product A which boils above the Diesel fuel boiling range. In yet another particular a embodiment, the heavy product stream D comprises the fraction of the oligomerisation product A which boils above the jet fuel boiling range.

The middle distillate products stream C comprises a fraction of the oligomerisation product A which has a lower boiling point which is above the C8 mono-olefin boiling point range and an upper boiling point which is up to the C22 mono-olefin boiling point range. In another embodiment, the middle distillate products stream C contains the fraction of the oligomerisation product A which boils in the temperature range have a lower limit selected from any one of the following: 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 200 °C, 220 °C and 250 °C; and an upper limit selected from any one of the following: 350 °C, 330 °C, 320 °C, 310 °C, 290 °C, 280 °C, 270 °C, 260 °C and 250 °C; with the proviso that there is at least a 10 °C difference between the lower and upper limit in the temperature range.

In one embodiment of the present invention, the light products stream B will consist of the fraction which is separated in step (b) of the process which has boiling point lower than the boiling point range of the middle distillate products stream C, and the heavy products stream D will consist of the fraction which is separated in step (b) of the process which has boiling point higher than the boiling point range of the middle distillate products stream C. Thus, in one embodiment of the present invention, the separation of the light

products stream B, the middle distillate products stream C and the heavy products stream D in step (b) will be performed such that the upper boiling point limit of the lights product stream B will be the same as the lower boiling point limit of the middle distillate products stream C and the lower boiling point limit of the heavy products stream D will be the same as the upper boiling point limit of the middle distillate products stream C.

It will be understood by a skilled person that due to the process of fractionation of hydrocarbon streams, such as those produced in the process of the present invention, may result in small amounts of hydrocarbon compounds having boiling points outside of the range selected; for instance, whilst a distillation column or flash vessel may be operated to separate a hydrocarbon stream in to a lighter fraction having a boiling point of at most 180 °C and a heavier fraction having a boiling point of at least 180 °C, the lighter fraction may contain small amounts hydrocarbon compounds which have a boiling point greater than 180 °C and the heavier fraction may contain small amounts hydrocarbon compounds which have a boiling point lower than 180 °C. Thus, when referring to upper boiling points, lower boiling points and boiling point ranges in the present invention, it is meant that at least 90 wt%, preferably at least 95 wt%, of the fraction boils above the specified lower boiling point limit and/or below the specified upper boiling point limit, or at least 80 wt%, preferably at least 90 wt%, of the fraction boils within the specified boiling point range.

The means of separation of the light products stream B, the middle distillate products stream C and the heavy products stream D, in step (b), is not limited. In one embodiment of the present invention, the separation performed in step (b) is performed in a single distillation column. In another embodiment of the present invention, the separation performed in step (b) is performed in a series of two or more distillation columns. In another embodiment of the present invention, the separation performed in step (b) is performed in a series of two or more flash distillation vessels. In another embodiment of the present invention, the separation performed in step (b) is performed in a system which comprises at least one flash distillation vessel and at least one distillation column.

Thus, in a specific embodiment of the process of the present invention, step (b) is performed in a single distillation column with a three effluent streams: light products stream B, middle distillate products stream C and heavy products stream D.

In another specific embodiment of the process of the present invention, step (b) is

performed by a process comprising at least the following steps:

(i) separating the light products stream B from the oligomerisation product A to produce a combined middle distillate and heavy stream G, and

5 (ii) separating the middle distillate product stream C and the heavy products stream D from the combined middle distillate and heavy stream G.

The means of separation for each of steps (i) and (ii) of this process are not limited, and each step may be performed in one or more distillation columns and/or flash distillation vessels.

10 Thus, when step (b) of the process of the present invention is performed by a process comprising at least steps (i) and (ii) as described above, the overall process for the preparation of a middle distillate hydrocarbon composition from ethylene comprises the following steps:

(a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A,
15 wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;

(b-i) separating the light products stream B from the oligomerisation product A to produce a combined middle distillate and heavy stream G, wherein the light product stream B comprises the fraction of oligomerisation product A which boils
20 in the C2-C8 mono-olefin boiling range and the combined middle distillate and heavy stream G comprises the fraction of oligomerisation product A which boils above the boiling range of the light product stream B;

(b-ii) separating a middle distillate product stream C and a heavy products stream D from the combined middle distillate and heavy stream G, wherein the middle
25 distillate product stream C comprises a fraction of the combined middle distillate and heavy stream G which boils below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of the combined middle distillate and heavy stream G which boils above the C22 mono-olefin boiling range;

30 (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;

(d) cracking the heavy product stream D in a cracking reactor to produce a cracked

product stream E;

(e) separating a middle distillate product F from the cracked product stream E; and

(f) hydrogenating the middle distillate product stream C,

wherein the middle distillate hydrocarbon composition comprises at least a portion of
5 the hydrogenated middle distillate product stream C and at least a portion of the middle
distillate product F.

In the process of the present invention, the middle distillate product stream C is
subjected to a hydrogenation process in order to reduce the level of olefinic unsaturation in
the final middle distillate hydrocarbon composition compared to the middle distillate
10 product stream C or to remove the olefinic unsaturation in the middle distillate
hydrocarbon composition.

Therefore, in step (f) of the present invention, the middle distillate product stream C
is hydrogenated by any known hydrogenation process. Typically, the hydrogenation
process will comprise contacting the middle distillate product stream C with hydrogen-rich
15 gas in the presence of a suitable hydrogenation catalyst under hydrogenation reaction
conditions.

Examples of suitable hydrogenation catalysts include catalysts based on Group VIII
metals, in particular catalysts based on nickel, palladium, platinum, rhodium and
ruthenium.

20 In one embodiment, the hydrogenation catalyst is a catalysts comprises a metal
selected from palladium and nickel, on a support comprising alumina, silica or silica-
alumina. In this embodiment, the metal content of the catalyst will typically be in the
range of from 0.1 to 10 wt% for palladium and in the range of from 1 to 60 wt% for nickel.
In this embodiment, the operating conditions typically comprise a liquid hourly space
25 velocity of from 1 to 8 h⁻¹, a temperature in the range of from 100 to 250 °C at the
hydrogenation reactor inlet and a pressure of from 2 to 5 MPa.

The extent to which the middle distillate product stream C is hydrogenated will
depend upon the desired use of the middle distillate hydrocarbon composition. In one
particular embodiment where the middle distillate hydrocarbon composition is intended for
30 use as, or in, Diesel fuels or for use as, or in, jet fuels, it is preferred that the bromine
number of the middle distillate product stream is reduced to at most 1 g Br/100 g
(ASTM D1159).

In the embodiment wherein step (b) is performed by a process comprising at least steps (i) and (ii) indicated herein, the combined middle distillate and heavy stream G may optionally be subjected to a hydrogenation process prior to step (ii). When the combined middle distillate and heavy stream G is subjected to a hydrogenation process, said stream
5 may be hydrogenated by any known hydrogenation process. Typically, the hydrogenation process will comprise contacting the combined middle distillate and heavy stream G with hydrogen-rich gas in the presence of a suitable hydrogenation catalyst under hydrogenation reaction conditions. Examples of suitable catalysts and process would be known to one skilled in the art, such as those processes described in relation to step (f), which are
10 explicitly included in this embodiment.

In the embodiment wherein step (b) is performed by a process comprising at least steps (i) and (ii) indicated herein, the hydrogenation of the middle distillate product stream C (referred to as step (f) in the first embodiment of the invention) may be performed on the middle distillate product stream C prior to the separation of the middle distillate product
15 stream C and the heavy product stream D in step (ii); namely, the hydrogenation step is performed on the combined middle distillate and heavy stream G.

Therefore, in one particular embodiment of the present invention there is provided a process for the preparation of a middle distillate hydrocarbon composition from ethylene comprises the following steps:

- 20 (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
- (b-i) separating the light products stream B from the oligomerisation product A to
25 produce a combined middle distillate and heavy stream G, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the combined middle distillate and heavy stream G comprises the fraction of oligomerisation product A which boils above the boiling range of the light product stream B;
- 30 (b-ii) hydrogenating the combined middle distillate and heavy stream G;
- (b-iii) separating a hydrogenated middle distillate product stream C and a heavy products stream D from the combined middle distillate and heavy stream G, wherein the

- hydrogenated middle distillate product stream C comprises a fraction of the combined middle distillate and heavy stream G which boils below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of the combined middle distillate and heavy stream G which boils above the C22 mono-olefin boiling range;
- 5
- (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
 - (d) cracking the heavy product stream D in a cracking reactor to produce a cracked product stream E; and
 - 10 (e) separating a middle distillate product F from the cracked product stream E;
- wherein the middle distillate hydrocarbon composition comprises at least a portion of the hydrogenated middle distillate product stream C and at least a portion of the middle distillate product F.

In the present invention, at least a portion of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process. In one particular

15 embodiment, all of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process; in this embodiment, the removal of a purge stream to prevent build-up of products boiling below the boiling point of ethylene and other unreactive or otherwise undesirable components is permissible. In another embodiment,

20 part of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process and another part of the light products stream B is separated as a separate product composition. In yet a further embodiment, part of the light products stream B is recycled back to the oligomerisation reaction zone of step (a) of the process and another part of the light products stream B is separated and used as fuel to provide heat

25 energy to one or more parts of the process or processes upstream or downstream of the process of the present invention; such as preheating and vapourising ethanol which is to be dehydrated or providing heat energy to a separation, cracking, hydrogenation or optional dehydration process.

Any components in the oligomerisation product A which may be present and have a

30 boiling point below the boiling point of ethylene (-103.7 °C at atmospheric pressure (1.013 bar)) will typically be included in the light products fraction. To prevent build-up of any components having a boiling point below the boiling point of ethylene or any inert

compounds, such as alkanes, in the oligomerisation process, part of light products stream B may be purged during the step of recycling at least part of the light products stream B.

In the process of the present invention, the heavy products stream D is subjected to a cracking process to produce a cracked product stream E.

5 Therefore, in step (d) of the present invention, the heavy products stream D is cracked by any known cracking process. Examples of suitable cracking processes which may be employed in the process of the present invention include thermal cracking, steam cracking, catalytic cracking and hydrocracking, with hydrocracking being preferred.

10 In one particular embodiment, the heavy products stream D is subjected to a thermal cracking process to produce cracked product stream E. Suitable conditions for thermal cracking would be known to a person skilled in the art.

In one particular embodiment, the heavy products stream D is subjected to a steam cracking process to produce cracked product stream E. Suitable conditions for steam cracking would be known to a person skilled in the art.

15 In another particular embodiment, the heavy products stream D is subjected to a catalytic cracking process to produce cracked product stream E. Typically, the catalytic cracking process will comprise contacting the heavy products stream D with a suitable catalyst for catalytic cracking under catalytic cracking reaction conditions. Suitable catalysts and conditions for catalytic cracking would be known to a person skilled in the
20 art. Examples of suitable catalysts for catalytic cracking include catalysts containing alumina and catalysts containing zeolites.

In a particular preferred embodiment, the heavy products stream D is subjected to a hydrocracking process to produce cracked product stream E. Typically, the hydrocracking process will comprise contacting the heavy products stream D with hydrogen-rich gas in
25 the presence of a suitable hydrocracking catalyst under hydrocracking reaction conditions. Suitable catalysts and conditions for hydrocracking would be known to a person skilled in the art.

Examples of suitable hydrocracking catalysts include catalysts based on nickel on silica-alumina, nickel and tungsten on silica and alumina and palladium on zeolites.

30 A middle distillate product F is separated from the cracked product stream E. The middle distillate product F has the same boiling point characteristics as the middle distillate product stream C, namely it comprises a fraction of the cracked product stream E which

has a lower boiling point which is above the C8 mono-olefin boiling point range and an upper boiling point which is below the C22 mono-olefin boiling point range. In another embodiment, the middle distillate products F contains the fraction of the cracked product stream E which boils in the temperature range have a lower limit selected from any one of the following: 130 °C, 140 °C, 150 °C, 160 °C, 170 °C, 180 °C, 200 °C, 220 °C and 250 °C; and an upper limit selected from any one of the following: 350 °C, 330 °C, 320 °C, 310 °C, 290 °C, 280 °C, 270 °C, 260 °C and 250 °C; with the proviso that there is at least a 10 °C difference between the lower and upper limit in the temperature range.

The separation of the middle distillate product F from the cracked product stream E may be conducted in the same separation means as provided in step (b) of the process, may be conducted in part in a separate separation means and in part the same separation means as provided in step (b) of the process, or it may be conducted entirely in a separate separation means. Preferably, the separation of the middle distillate product F from the cracked product stream E is conducted entirely in a separate separation means or in part in a separate separation means and in part the same separation means as provided in step (b) of the process.

In the embodiment wherein the separation of the middle distillate product F from the cracked product stream E is conducted in the same separation means as provided in step (b), the cracked product stream E is recycled to step (b) and the separation of middle distillate product F from the cracked product stream E of the step (e) and the separation of the middle distillate product stream C is performed in the same separation step.

Thus, when the separation of the middle distillate product F from the cracked product stream E is conducted in the same separation means as provided in step (b), the overall process for the preparation of a middle distillate hydrocarbon composition from ethylene comprises the following steps:

- (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
- (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light

- product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range;
- 5
- (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
 - 10 (d) cracking the heavy product stream D in a cracking reactor to produce a cracked product stream E;
 - (e) recycling the cracked product stream E to step (b); and
 - (f) hydrogenating the middle distillate product stream C,
- wherein the middle distillate hydrocarbon composition comprises at least a portion of
- 15 the hydrogenated middle distillate product stream C.

However, depending upon the type and severity of cracking performed on the heavy product stream D in step (d) of the process of the present invention, the cracked product stream E may comprise substantial amounts of non-olefinic hydrocarbons which have a boiling point below the boiling point of the middle distillate product F. In such cases,

20 recycling the entire cracked product stream back to the separation step (b) would result in the build-up of such non-olefinic hydrocarbons in the light products stream B, and consequently in the oligomerisation reaction zone. Therefore, to avoid such a build-up of such non-olefinic hydrocarbons in the light products stream B, the cracked product stream E is preferably subjected to a separate separation step in which a naphtha product which

25 comprises the fraction of the cracked product stream E which boils below the lower boiling point of the middle distillate product stream C is removed. The remaining fraction of the cracked product stream E may then conveniently be recycled back to the separation means of step (b) of the process to enable the separation of middle distillate product F from the remaining fraction of the cracked product stream E and the separation of the middle

30 distillate product stream C from oligomerisation product A to be performed in the same separation step.

Thus, in one particular embodiment, the separation of the middle distillate product F

is performed in a two-step process, wherein the first step comprises separating a naphtha product which comprises the fraction of the cracked product stream E which boils below the lower boiling point of the middle distillate product stream C from cracked product stream E, followed by recycling the remaining fraction of cracked product stream E to step 5 (b) wherein the separation of the middle distillate product F occurs at the same time and in the same separation means as the separation of the middle distillate product stream C.

Thus, when a naphtha product is separated from the cracked product stream E and the separation of the middle distillate product F from the remaining portion of the cracked product stream E is conducted in the same separation means as provided in step (b), the overall process for the preparation of a middle distillate hydrocarbon composition from 10 ethylene comprises the following steps:

- (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of 15 from 30 to 300 °C and a pressure of at least 10 bara;
- (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the middle distillate product stream C 20 comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range;
- (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
- (d-i) cracking the heavy product stream D in a cracking reactor to produce a cracked product stream E;
- (d-ii) separating a naphtha product which comprises the fraction of the cracked product 30 stream E which boils below the lower boiling point of the middle distillate product stream C from cracked product stream E;
- (e) recycling the remaining fraction of cracked product stream E to step (b); and

(f) hydrogenating the middle distillate product stream C,
wherein the middle distillate hydrocarbon composition comprises at least a portion of
the hydrogenated middle distillate product stream C.

Alternatively, when a naphtha product is separated from the cracked product stream
5 E and the separation of the middle distillate product F from the remaining portion of the
cracked product stream E is conducted in the same separation means as provided in step
(b), and said separation is conducted in a process comprising at least steps (i) and (ii), the
overall process for the preparation of a middle distillate hydrocarbon composition from
ethylene comprises the following steps:

- 10 (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a
supported nickel oligomerisation catalyst to form an oligomerisation product A,
wherein the oligomerisation reaction is operated at a temperature in the range of
from 30 to 300 °C and a pressure of at least 10 bara;
- (b-i) separating the light products stream B from the oligomerisation product A to
15 produce a combined middle distillate and heavy stream G, wherein the light
product stream B comprises the fraction of oligomerisation product A which boils
in the C2-C8 mono-olefin boiling range and the combined middle distillate and
heavy stream G comprises the fraction of oligomerisation product A which boils
above the boiling range of the light product stream B;
- 20 (b-ii) separating a middle distillate product stream C and a heavy products stream D
from the combined middle distillate and heavy stream G, wherein the middle
distillate product stream C comprises a fraction of the combined middle distillate
and heavy stream G which boils below the boiling range of the heavy products
stream D, and wherein the heavy product stream D comprises the fraction of the
25 combined middle distillate and heavy stream G which boils above the C22 mono-
olefin boiling range;
- (c) recycling at least a portion of the light products stream B to the oligomerisation
reaction zone of step (a) of the process;
- (d-i) cracking the heavy product stream D in a cracking reactor to produce a cracked
30 product stream E;
- (d-ii) separating a naphtha product which comprises the fraction of the cracked product
stream E which boils below the lower boiling point of the middle distillate product

stream C from cracked product stream E;

(e) recycling the remaining fraction of product stream E to step (b-ii); and

(f) hydrogenating the middle distillate product stream C,

5 wherein the middle distillate hydrocarbon composition comprises at least a portion of the hydrogenated middle distillate product stream C.

In the embodiment wherein the separation of the middle distillate product F from the cracked product stream E is conducted in a separate separation means to the separation means provided in step (b), the means of separation of the middle distillate product F from the cracked product stream E is not limited; for example, the separation may be performed
10 in a single distillation column, in a single flash distillation vessel, in a series of two or more distillation columns, in a series of two or more flash distillation vessels, or . in a system which comprises at least one flash distillation vessel and at least one distillation column.

In the embodiments wherein the separation of the middle distillate product F from the cracked product stream E is conducted in a separate separation means to the separation
15 means provided in step (b), the cracked product stream E is separated in to a naphtha product, the middle distillate product F and a remaining heavy product, wherein the naphtha product consists of the fraction of the cracked product stream E which boils below the middle distillate product F and the remaining heavy product consists of the fraction of
20 the cracked product stream E which boils above the middle distillate product F. The remaining heavy product from the cracked product stream E may conveniently be recycled back to the cracking reactor in step (d) of the process.

In the embodiment wherein the separation of the middle distillate product F from the cracked product stream E is conducted in a separate separation means to the separation
25 means provided in step (b), at least part of the middle distillate product F may be combined with the middle distillate product stream C prior to step (f), and/or at least part of the middle distillate product F may be combined with the hydrogenated middle distillate product stream C.

Conveniently, when hydrocracking is used in step (d) of the process, the middle
30 distillate product F already comprises a majority of alkanes. Thus, when hydrocracking is used in step (d) of the process, the middle distillate product F is preferably combined with the hydrogenated middle distillate product stream C.

The middle distillate hydrocarbon composition of the present invention comprises at least a portion of the hydrogenated middle distillate product stream C and at least a portion of the middle distillate product F.

5 In one embodiment, all of the hydrogenated middle distillate product stream C and all of the middle distillate product F are combined to form the middle distillate hydrocarbon composition of the present invention.

In another embodiment of the present invention, a portion of the hydrogenated middle distillate product stream C is combined with all of the middle distillate product F to form the middle distillate hydrocarbon composition.

10 In another embodiment of the present invention, all of the hydrogenated middle distillate product stream C is combined with a portion of the middle distillate product F to form the middle distillate hydrocarbon composition.

15 It is within the scope of the present invention that further fractionation of the hydrogenated middle distillate product stream C and/or the middle distillate product F may optionally occur prior to combining the streams, or portions thereof, to form the middle distillate hydrocarbon composition.

The middle distillate hydrocarbon composition may conveniently be used as a fuel per se, or may be used as a component in a fuel. In particular, the middle distillate hydrocarbon composition prepared by the process of the present invention is particularly
20 suitable for use as a Diesel fuel or as a component in a Diesel fuel; as a jet fuel or as a component in a jet fuel; as a marine or static engine fuel or as a component in a marine or static engine fuel; as a fuel for a turbine engine or as a component in a fuel for a turbine engine; as a heating fuel or as a component in a heating fuel; and, as a lamp oil or as a component in a lamp oil.

25 Since the middle distillate hydrocarbon composition will contain extremely low levels of compounds which are not hydrocarbons, if any, the middle distillate hydrocarbon composition may conveniently be used to upgrade fuels which contain levels of impurities which are considered too high.

30 Furthermore, due to the nature of the oligomerisation process in the process of the present invention, the middle distillate hydrocarbon composition will contain a significant amount of branched hydrocarbons. Therefore, conveniently, the middle distillate hydrocarbon composition prepared by the process of the present invention may

advantageously have a lower pour point temperature and/or a lower cloud point temperature than equivalent fractions of oligomeric products which have been derived from processes which form predominantly linear hydrocarbons.

In one embodiment of the present invention, the middle distillate hydrocarbon composition is a hydrocarbon composition boiling in the Diesel fuel boiling range. In this embodiment, the middle distillate hydrocarbon composition may be used as a Diesel fuel per se, or may be used as a component in a Diesel fuel. Should the middle distillate hydrocarbon composition be used as a component in a Diesel fuel, then said middle distillate hydrocarbon composition may be blended with any formulated Diesel fuel or Diesel fuel base stock; for instance the middle distillate hydrocarbon composition may be blended with a Diesel fuel or Diesel fuel base stock which has been derived from crude oil, from a Fischer-Tropsch process, from a biological source (also referred to as biodiesel), or from combinations thereof. Advantageously, if the middle distillate hydrocarbon composition is prepared from ethylene which has been derived from the dehydration of bioethanol, then the middle distillate hydrocarbon composition may provide an additional source of biologically derived Diesel fuel or component thereof to the finished Diesel fuel.

In one embodiment of the present invention, the middle distillate hydrocarbon composition is a hydrocarbon composition boiling in the jet fuel boiling range. In this embodiment, the middle distillate hydrocarbon composition may be used as a jet fuel per se, or may be used as a component in a jet fuel. Should the middle distillate hydrocarbon composition be used as a component in a jet fuel, then said middle distillate hydrocarbon composition may be blended with any formulated jet fuel or jet fuel base stock; for instance the middle distillate hydrocarbon composition may be blended with a jet fuel or jet fuel base stock which has been derived from crude oil, from a Fischer-Tropsch process, from a biological source, or from combinations thereof. Advantageously, if the middle distillate hydrocarbon composition is prepared from ethylene which has been derived from the dehydration of bioethanol, then the middle distillate hydrocarbon composition may provide an additional source of biologically derived jet fuel or component thereof to the finished jet fuel.

In one embodiment of the present invention, the middle distillate hydrocarbon composition is a hydrocarbon composition boiling in the heating fuel boiling range. In this embodiment, the middle distillate hydrocarbon composition may be used as a heating fuel

per se, or may be used as a component in a heating fuel. Should the middle distillate hydrocarbon composition be used as a component in a heating fuel, then said middle distillate hydrocarbon composition may be blended with any formulated heating fuel or heating fuel base stock; for instance the middle distillate hydrocarbon composition may be blended with a heating fuel or heating fuel base stock which has been derived from crude oil, from a Fischer-Tropsch process, from a biological source, or from combinations thereof. Advantageously, if the middle distillate hydrocarbon composition is prepared from ethylene which has been derived from the dehydration of bioethanol, then the middle distillate hydrocarbon composition may provide an additional source of biologically derived heating fuel or component thereof to the finished heating fuel.

In one embodiment of the present invention, the middle distillate hydrocarbon composition is a hydrocarbon composition boiling in the lamp oil boiling range. In this embodiment, the middle distillate hydrocarbon composition may be used as a lamp oil per se, or may be used as a component in a lamp oil. Should the middle distillate hydrocarbon composition be used as a component in a lamp oil, then said middle distillate hydrocarbon composition may be blended with any formulated lamp oil or lamp oil base stock; for instance the middle distillate hydrocarbon composition may be blended with a lamp oil or lamp oil base stock which has been derived from crude oil, from a Fischer-Tropsch process, from a biological source, or from combinations thereof. Advantageously, if the middle distillate hydrocarbon composition is prepared from ethylene which has been derived from the dehydration of bioethanol, then the middle distillate hydrocarbon composition may provide an additional source of biologically derived lamp oil or component thereof to the finished lamp oil.

Therefore, the present invention also provides a Diesel fuel composition comprising a Diesel fuel base stock and a middle distillate hydrocarbon composition boiling in the Diesel fuel boiling range prepared according to the process of the present invention, wherein the Diesel fuel base stock is selected from a Diesel fuel base stock derived from crude oil, a Fischer-Tropsch derived Diesel fuel base stock, a biodiesel and mixtures thereof.

The present invention yet further provides a jet fuel composition comprising a jet fuel base stock and a middle distillate hydrocarbon composition boiling in the jet fuel boiling range prepared according to the process of the present invention, wherein the jet

fuel base stock is selected from a jet fuel base stock derived from crude oil, a Fischer-Tropsch derived jet fuel base stock and mixtures thereof.

The present invention yet further provides a heating fuel composition comprising a heating fuel base stock and a middle distillate hydrocarbon composition boiling in the heating fuel boiling range prepared according to the process of the present invention, wherein the heating fuel base stock is selected from a heating fuel base stock derived from crude oil, a Fischer-Tropsch derived heating fuel base stock and mixtures thereof.

The present invention yet further provides a lamp oil composition comprising a lamp oil base stock and a middle distillate hydrocarbon composition boiling in the lamp oil boiling range prepared according to the process of the present invention, wherein the lamp oil base stock is selected from a lamp oil base stock derived from crude oil, a Fischer-Tropsch derived lamp oil base stock and mixtures thereof.

Examples

Preparation of Catalyst

Davicat 3125 (Trade Mark) silica-alumina powder (50 g), supplied by Grace Davison, was weighed into a 500 mL round bottomed flask. A solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (9.51 g) in water (150 mL) was added, and the mixture refluxed for 4 hours with stirring. After cooling, the suspension was filtered and washed extensively with deionised water using vacuum filtration. The resulting solid was dried in an oven at 110 °C for 18 hours. Analysis showed that the product contained 2.1 wt% nickel.

The catalysts used in the testing were of a 125-160 µm particle size. To form the catalysts of the specified particle size, the dried solid was pelletised using a KBr press (press force 10 t, tool diameter 13 mm); the pelletised solid was then crushed with a mortar and pestle and pressed through a series of 1000 µm, 500 µm, 250 µm and finally through a 160 µm sieves. Shaking on a sieving device for 10 min at 70 Hz yielded the corresponding particle size fractions.

Catalyst testing

Two reactors tubes of 4.5 mm diameter were filled with an amount of catalyst equivalent to a dry weight of (a) 0.5 g and (b) 0.25 g. The dry weight of the catalyst was determined by LOI (loss of ignition) tests at 300 °C.

The catalysts were activated by heating at 300 °C for 3 hours under pure N_2 (3.1 NL/h to each reactor) to purge the catalyst bed free from air and residual moisture.

The reactor tube pressure was then set to 39 bar and temperature to 120 °C and a gas mixture comprising 10.2 mol% Ar and 89.8 mol% dry C₂ H₄ was passed through each reactor tube, such that the feed rates of the components of the mixture to each tube were 75 normal cm³/hour for argon and 656 normal cm³/hour for ethylene, where “normal cm³/hour is the volume that would be used if the gases were a atmospheric pressure.

For each reactor tube, the product stream leaving the reactor tube was mixed with nitrogen and passed through a condenser vessel at 110 °C to collect liquid products. After 24 hours of operation the liquids were collected and analysed for olefin content. The gases leaving each reactor tube at this time were also analysed for olefin content. The data shown in Figure 1 gives the combined analytical results as mass% of total hydrocarbon product for the gas and liquid streams.

The two reactor tubes contained the same catalyst, with 0.25 g and 0.5 g. Consequently, the analysis of the product from the reactor tube containing 0.25 g catalyst is an indication of the composition at the midpoint of the catalyst bed in the reactor tube containing 0.5 g catalyst. The product composition leaving the reactor tube with 0.5 g and the product composition at the midpoint of the catalyst bed allow the extent of reaction in the first and second halves of the catalyst bed to be compared.

Thus, at the midpoint of the catalyst bed, all of the ethylene feed has been consumed. In the second half of the catalyst bed, the concentration of C₄, C₆ and C₈ olefins decreases, while the concentration of heavier olefins increases. This indicates that at least the C₄, C₆ and C₈ olefins are reacted and converted into heavier olefins in the presence of the catalyst under the reaction conditions.

Claims

1. A process for the preparation of a middle distillate hydrocarbon composition from ethylene, wherein said process comprises the following steps:

- 5 (a) feeding an ethylene composition in to an oligomerisation reaction zone containing a supported nickel oligomerisation catalyst to form an oligomerisation product A, wherein the oligomerisation reaction is operated at a temperature in the range of from 30 to 300 °C and a pressure of at least 10 bara;
- 10 (b) separating a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A, wherein the light product stream B comprises the fraction of oligomerisation product A which boils in the C2-C8 mono-olefin boiling range and the middle distillate product stream C comprises a fraction of oligomerisation product A which boils above the boiling range of the light product stream B and below the boiling range of the heavy products stream D, and wherein the heavy product stream D comprises the fraction of oligomerisation product A which boils above the C22 mono-olefin boiling range;
- 15 (c) recycling at least a portion of the light products stream B to the oligomerisation reaction zone of step (a) of the process;
- (d) cracking the heavy product stream D in a cracking reactor to produce a cracked product stream E;
- 20 (e) separating a middle distillate product F from the cracked product stream E; and
- (f) hydrogenating the middle distillate product stream C,

wherein the middle distillate hydrocarbon composition comprises at least a portion of the hydrogenated middle distillate product stream C and at least a portion of the middle distillate product F.

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2. A process according to claim 1, wherein in step (d) the heavy products stream D is subjected to a hydrocracking process to produce cracked product stream E.

3. A process according to claim 1 or claim 2, wherein the separation of the middle distillate product F is performed in a two-step process, wherein the first step comprises separating a naphtha product which comprises the fraction of the cracked product stream E which boils below the lower boiling point of the middle distillate product stream C from cracked product stream E, followed by recycling the remaining fraction of cracked product

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stream E to step (b) wherein the separation of the middle distillate product F occurs at the same time and in the same separation means as the separation of the middle distillate product stream C.

4. A process according to claim 1 or claim 2, wherein in step (e) the cracked product stream E is separated in to a naphtha product, the middle distillate product F and a remaining heavy product, wherein the naphtha product consists of the fraction of the cracked product stream E which boils below the middle distillate product F and the remaining heavy product consists of the fraction of the cracked product stream E which boils above the middle distillate product F.
5. A process according to claim 4, wherein the remaining heavy product is recycled back to step (b).
6. A process according to any one of claims 1 to 5, wherein the separation of a light products stream B, a middle distillate product stream C and a heavy products stream D from oligomerisation product A of step (b) is performed by a process comprising at least the following steps:
 - (i) separating the light products stream B from the oligomerisation product A to produce a combined middle distillate and heavy stream G, and
 - (ii) separation the middle distillate product stream C and the heavy products stream D from the combined middle distillate and heavy stream G.
7. A process according to claim 6, wherein the combined middle distillate and heavy stream G is subjected to a hydrogenation process prior to step (ii).
8. A process according to claim 6, wherein the hydrogenation step (f) is performed on the combined middle distillate and heavy stream G prior to step (ii).
9. A process according to any one of claims 6 to 8, wherein in step (e) the cracked product stream E is separated in to a naphtha product, the middle distillate product F and a remaining heavy product, wherein the naphtha product consists of the fraction of the cracked product stream E which boils below the middle distillate product F and the remaining heavy product consists of the fraction of the cracked product stream E which boils above the middle distillate product F, and wherein the remaining heavy product is combined with the combined middle distillate and heavy stream G after step (i).
10. A process according to claim 9, wherein the combined remaining heavy product and combined middle distillate and heavy stream G is subjected to a hydrogenation process

prior to step (ii).

11. A process according to claim 9, wherein the hydrogenation step (f) is performed on the combined remaining heavy product and combined middle distillate and heavy stream G prior to step (ii).

5 12. A process according to any one of claims 1 to 11, wherein the oligomerisation catalyst comprises an amorphous silica-alumina support.

13. A process for the preparation of a middle distillate hydrocarbon composition from ethanol, wherein said process comprises the following steps:

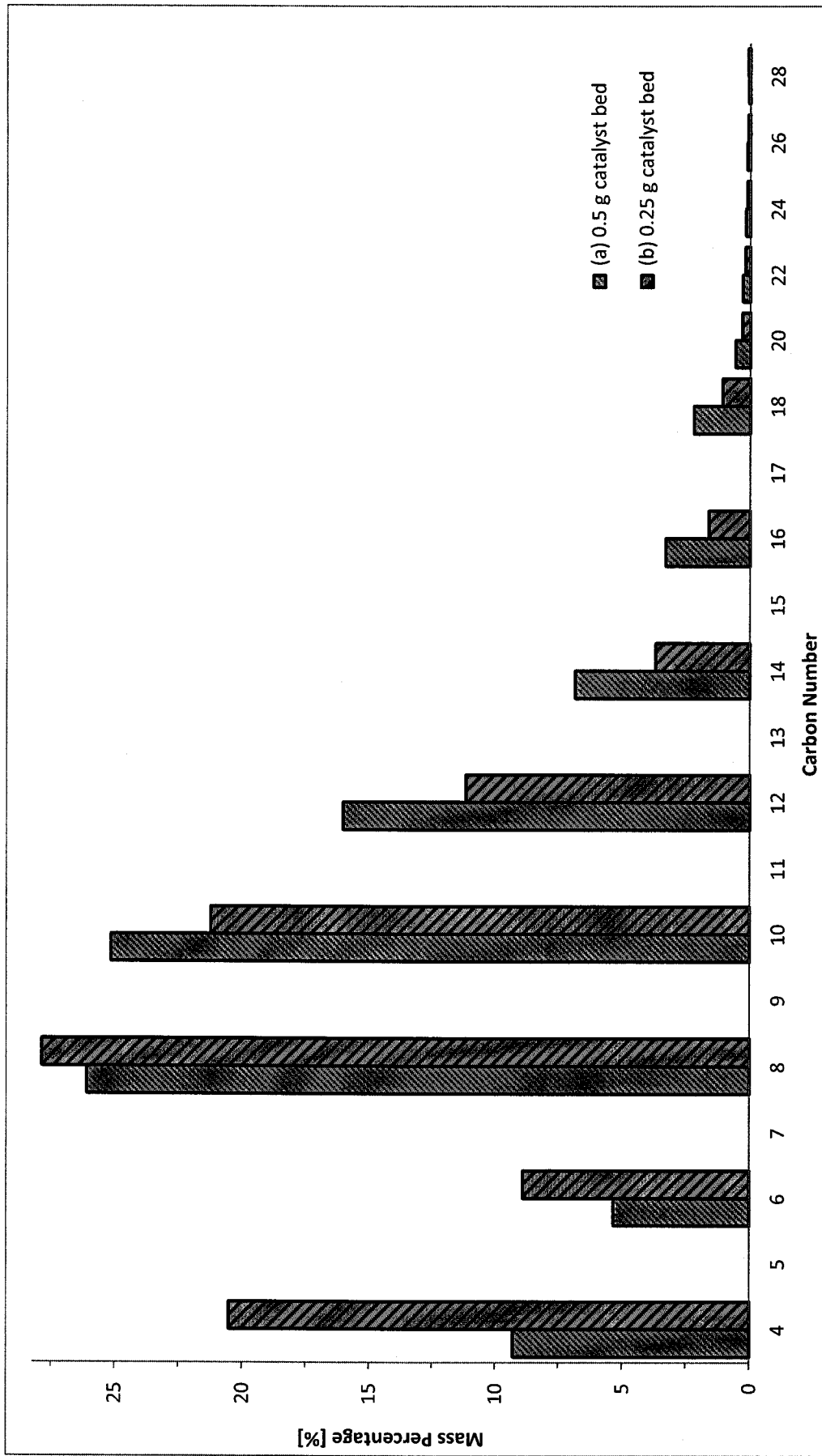
- 10 (1) feeding an ethanol composition to a dehydration reactor containing an ethanol dehydration catalyst, wherein the dehydration reactor is operated at a temperature and pressure effective to dehydrate at least part of the ethanol to ethylene and water;
- (2) separating a stream comprising ethylene from the effluent of the dehydration reactor of step (1);
- 15 (3) subjecting the stream comprising ethylene from step (2) to a process for removing any water, alcohols or other oxygenates which may be present to form an ethylene composition; and
- (4) preparing the middle distillate hydrocarbon composition from the ethylene composition stream from step (3) in accordance with the process of any one of
20 claims 1 to 12.

14. A Diesel fuel composition comprising a Diesel fuel base stock and a middle distillate hydrocarbon composition boiling in the Diesel fuel boiling range prepared according to any one of claims 1 to 13, and, wherein the Diesel fuel base stock is selected from a Diesel fuel base stock derived from crude oil, a Fischer-Tropsch derived Diesel fuel
25 base stock, a biodiesel and mixtures thereof.

15. A jet fuel composition comprising a jet fuel base stock and a middle distillate hydrocarbon composition boiling in the jet fuel boiling range prepared according to any one of claims 1 to 13, wherein the jet fuel base stock is selected from a jet fuel base stock derived from crude oil, a Fischer-Tropsch derived jet fuel base stock and mixtures thereof.

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Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/056152

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10G47/00 C10G50/00 C10G65/14 C10G69/00 C10G69/12
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C10G
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

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Y	claims 1-12 figure 1 page 11, lines 24-33 page 16, lines 9-13 pages 18-20 ----- -/--	1-13

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 6 May 2014	Date of mailing of the international search report 12/05/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Pardo Torre, J
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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