ESSENTIALLY HYDROCARBON COMPOSITIONS TO BE USED AS FuELS WITH ENHANCED LUBRICATION PROPERTIES

Inventors: Silvia Pavoni, Pietro (IT); Vincenzo Calemma, San Donato Milanese (IT)

Correspondence Address:
OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C.
1940 DUKE STREET
ALEXANDRIA, VA 22314 (US)

Assignees: ENI S.p.A., Rome (IT); ENITEC NOLOGIE S.p.A., San Donato Milanese (IT)

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ABSTRACT

An essentially hydrocarbon composition comprising a refinery liquid fuel and from 1 to 25% by weight of a medium distillate essentially without alcoholic oxygen obtained starting from the product of a Fischer-Tropsch-type synthesis. This composition surprisingly has enhanced lubricating properties with respect to both of the original components and can advantageous be used as a fuel for Diesel or turbine engines, with an evident decrease in wear of the mobile parts in contact therewith.
ESSENTIALLY HYDROCARBON COMPOSITIONS TO BE USED AS FUELS WITH ENHANCED LUBRICATING PROPERTIES

[0001] The present invention relates to an essentially hydro-carbon composition having enhanced lubricating properties.

[0002] More specifically, the present invention relates to a hydrocarbon composition which can be used as a fuel, especially for Diesel-type engines, which has surprisingly enhance lubricating properties with respect to the single original components, and maintains however a high cetane number and a reduced presence of aromatics.

[0003] Fuels for Diesel engines are characterized by various properties associated both with their performances in the combustion phase and also with their cold flow properties and lubrication. In particular, it is important for the capacity of Diesel fuel to maintain lubricating properties which significantly reduce the wear of the mechanical parts involved in fluid transfer, such as pumps, valves and injectors. These lubricating properties are usually measured by means of specific empirical methods well known to experts in the field, such as the indication of the so-called lubricity according to the HFRR method (regulation CEC-F-06-A-96), to which reference is made hereunder in the present description.

[0004] The increasingly restrictive regulations on the characteristics of fuels for injection engines and turbines (Jet Fuel) generally aim at reducing the quantity of aromatic compounds and sulfur in order to maintain exhaust gas emissions within limits which are becoming stricter and stricter from an environmental point of view. One of the most commonly used methods for allowing a Diesel fuel to fall within these limits consists in effecting a more or less extensive hydrogenation thereof, which however has the disadvantage of significantly reducing its lubricating properties.

[0005] It is also known that certain mixtures of hydrocarbons within the distillation range of typical gas oil cuts for Diesel engines, i.e. comprised within 230 and 370°C, obtained starting from syn-gas according to a synthesis process of the Fischer-Tropsch type, followed by a hydrogenating-isomerizing treatment, have excellent combustion and cold flow properties, with a cetane number normally higher than 60 and up to values of 80 or over, and pour points lower than −30°C.

[0006] Processes of the Fischer-Tropsch type (hereafter indicated with the usual abbreviation F.T.) are known to be processes which allow gaseous mixtures containing hydrogen and carbon monoxide in ratios varying from 2:1 to 4:1 (syn-gas) to be converted into liquid or solid mixtures of essentially linear hydrocarbons, sometimes partially oxygenated. In addition to the process set up in its different modifications by Fischer and Tropsch in the 30s', all analogous processes which apply the same principle are included in the definition of F.T. processes, i.e. in general the direct synthesis of organic hydrocarbon or oxygenated products starting from suitable mixtures of hydrogen and carbon monoxide, in the presence of appropriate catalysts, specifically called F.T. catalysts.

[0007] Typical F.T. catalysts for obtaining prevalently paraffinic products with medium-high distillation ranges are based on cobalt or iron, generally supported on inert oxides such as alumina, silica and their mixtures. The molecular weight distribution in these liquid mixtures extends to a range of values which vary according to the catalyst and process conditions.

[0008] The paraffinic products obtained from the Fischer-Tropsch synthesis reactor are subsequently subjected to hydrogenating and/or isomerizing treatment (hydro-isomerization, hydrotreating, hydrocracking) in the presence of suitable catalysts, followed by fractionation by distillation to obtain fuel cuts within the desired range, usually medium distillates, i.e. gas oil and/or kerosene, commonly called Diesel Fuel and Jet Fuel.

[0009] These cuts (or fractions) deriving from F.T. processes therefore usually consist of mixtures of essentially paraffinic hydrocarbons, with distillation ranges (according to the publications) from 150-180 to 230-250 for Jet Fuel and from 230-260 to 360-380 for Diesel, wherein from 60 to 90% of the molecules have prevalently methyl branchings. Possible unsaturations or oxygenated groups, typically present in a quantity ranging from 5 to 10% by weight in the Fischer-Tropsch synthesis product, are normally removed during the treatment with hydrogen mentioned above.

[0010] The Diesel and/or Jet Fuel fractions obtained by the hydrocracking of F.T. waxes, under suitable conditions, as described, for example, in patent publications EP-A 1101813 and U.S. Pat. No. 6,310,108, have excellent properties at low temperatures. Furthermore, due to the lack of sulfated, nitrogenated and aromatic compounds, the medium distillates obtained by the hydrocracking of F.T. paraffins have an excellent performance with respect to their environmental impact, as specified, for example, in the article of Ref. T. W. Ryan "Emission performance of Fischer-Tropsch Diesel Fuel", Proceedings of the Conference on Gas Liquids Processing '99, May 17-19, 1999, S. Antonio, Tex. In the case of Diesel, the high hydrogen content produces lower flash points and consequently a lower emission of NOx. The lack of aromatic and sulfated compounds, moreover, leads to a drastic reduction in particulate emissions and facilitates the post-treatment of the gases discharged.

[0011] The lubricity of these mixtures or fractions is, on the contrary, normally unsatisfactory with values higher than 500 (measured according to the above HFRR method) far beyond the requisites of the regulations currently in force, which require values at least lower than 460.

[0012] The addition of certain additives to gas oil fraction or kerosene in order to increase the lubricating capacity, is also known. This technique is used both for traditional refinery fuels and also for those obtained by means of F.T. processes. Although satisfactory results have been obtained in terms of lubricity, the use of these additives causes a significant increase in the cost of the fuel, especially considering the necessity for selecting products essentially not containing sulfur or nitrogen. Furthermore, considerable corrosion phenomena on some parts of the engines fed with fuels containing these additives, have been observed after a period of time.

[0013] Diesel cuts deriving from F.T., which can be used as blending stocks suitable for improving the combustible properties and having high lubricating properties, are
described in U.S. Pat. No. 5,689,031. These hydrocarbon mixtures comprise a significant portion of oxygenated compounds and are obtained by means of a complex process which includes the separation of a fraction which is not subjected to hydrogenation treatment and subsequently joined to the remaining fraction subjected to hydro-isomerization. Although the diesel cut thus obtained has improved lubricating properties, its low temperature properties are not entirely satisfactory, and a costly and complex process is also required for its production.

[0014] There is consequently still a great request for improving the quality of fuels in so-called medium distillate cuts, and especially gas oil, in order to reduce the emissions of NOx and particulate in the discharge gases, at the same time maintaining good lubricating and cold flow properties and reducing the production costs.

[0015] The Applicant has now surprisingly found that by adding small quantities of a synthetic cut essentially without organic oxygen, deriving from a synthesis process of the Fischer-Tropsch type, to a traditional refinery medium distillate, especially gas oil, it is possible to obtain a combustible hydrocarbon composition having a higher lubricating capacity than that obtained from each of the original components, and also, with respect to the medium distillate, a much higher cetane number and an improved quality of the combustion emissions of an engine fed therewith.

[0016] A first object of the present invention therefore relates to a hydrocarbon composition which can be used as fuel for diesel or turbine engines, wherein at least 80% by weight, preferably 90% by weight has a distillation range comprised within 150 and 380°C, and which consists of a mixture of the following components:

[0017] A) from 80 to 99% by weight with respect to the overall weight of (A) and (B) of any refinery hydrocarbon mixture, having a distillation range comprised within 150 and 380°C,

[0018] B) from 1 to 20% by weight with respect to the overall weight of (A) and (B) of a hydrocarbon mixture essentially without oxygenated organic compounds, obtained by means of a process comprising a synthesis reaction of the Fischer-Tropsch type, having a distillation range comprised within 130 and 380°C, preferably comprised within 150 and 370°C.

[0019] Further objects of the present invention are evident from the following description and examples.

[0020] In order to clarify the description and claims of the present patent application and specify its relative scope, the meaning of some of the terms used herein is defined below:

[0021] the term “distillation range”, referring to a mixture of hydrocarbons, means, unless otherwise specified, the temperature or range of temperatures at the head of a typical distillation column from which said mixture is collected, at normal pressure (0.1009 MPa);

[0022] the definitions of the ranges always comprise the extremes, unless otherwise specified;

[0023] the term “hydrocracking”, as used herein with reference to any mixture or essentially hydrocarbon composition, generally means treatment with hydrogen of said mixture or composition, in the presence of a suitable catalyst, in order to obtain a product with a lower boiling point or range;

[0024] the terms “oxygen content”, referring to a prevalent hydrogen mixture or composition (hydrocarbons >70% by weight), and “oxygenated”, with reference to an organic compound, always refer to organic oxygen, i.e. bound to at least one carbon atom, therefore excluding any reference to water or other inorganic compounds containing oxygen;

[0025] the term “refinery”, as used herein referring to compositions or mixtures of combustible hydrocarbons, generally indicates compositions obtained from organic raw materials, especially of a mineral origin, by means of processing with transformation and purification processes typical of refineries, such as (hydro)cracking, reforming, hydrogenation, desulfurization, dewaxing, isomerization, distillation.

[0026] the term “distillation range comprised within two given temperatures”, with reference to compositions and mixtures mentioned in the present invention and claims, comprises all distillation ranges whose extremes are included within the two given temperatures. For example, limited to the definition of distillation range, a composition typically suitable as Diesel fuel, having a distillation range from 240 to 360°C, is included in the definition of compositions whose distillation range is comprised within 150 and 380°C.

[0027] Component (A) of the present composition can consist of any refinery hydrocarbon mixture having the characteristics specified above. Among these, those most suitable for use as fuels for engines are preferred, even though mixtures suitable for other uses are not excluded from the scope of the present invention. Hydrocarbon mixtures having a distillation range comprised within 200 to 370°C, particularly any non-synthetic gas oil fraction ranging from 240 to 360°C, are especially preferred.

[0028] Said mixtures of component (A) generally consist of aliphatic, naphthenic and aromatic hydrocarbons with varying structures and isomerization degrees, prevalently having a number of carbon atoms greater than 8 and up to about 30. Compounds containing hetero-atoms such as S, O, N, can also be present to a varying extent.

[0029] Refinery distillates containing the minimum possible quantity of hetero-atoms are however particularly suitable for the present invention, in accordance with the increasingly strict regulations aimed at reducing problems relating to the environmental impact of fuels. Medium distillates, and in particular gas oils, having an S content lower than 1000 ppm, preferably lower than 100 ppm, are particularly preferred. The lubricating properties of these products, in fact, progressively deteriorate with decreasing in the sulfur content, and have lubricity values corresponding to average diameters higher than 460 μm measured with the above HHRR method.

[0030] Typical but non-limiting examples of essentially hydrocarbon mixtures or fractions which can be used as component (A) in the compositions of the present invention are, for example, gas oil and kerosene from primary distil-
lution, gas oil and kerosene from desulfuration processes, gas oil from hydrocracking, gas oil from catalytic dewaxing.

Component (B) according to the present invention consists of a hydrocarbon mixture essentially without aromatic compounds and sulfur, and whose content of oxygenated compounds is lower than the minimum level which can be detected with the usual analytic methods, such as IR or NMR spectroscopy and gas-mass spectrometry. Said hydrocarbon mixture essentially consists of a mixture of linear and branched paraffins and is obtained by subjecting the product of an F.T. synthesis or a part thereof, to hydrogenating/isomerization treatment.

As already mentioned above, the latter product is usually characterized by a substantial absence of sulfur and preferably consists of over 70% by weight of linear paraffins having more than 15 carbon atoms. F.T. products are frequently solid or semi-solid at room temperature and for this reason are called waxes. Not all F.T. synthesis processes provide high-boiling mixtures of linear paraffins. Depending on the conditions used and the catalyst, the Fischer-Tropsch process can produce mixtures having different distillation temperature ranges, also relatively low if desired. It has proved to be more convenient however to carry out the process so as to prevalently obtain high-boiling mixtures or waxes, which can then be suitably degraded ad fractionated into the desired distillation cuts.

It is also known that F.T. processes produce hydrocarbon mixtures containing oxygenated hydrocarbons, normally in the form of alcohols, whose content can generally reach a maximum of 10% by weight with respect to the total.

If the F.T. process is carried out in the presence of catalysts based on cobalt, these oxygenated compounds mainly consist of alcohols with a linear chain, but can also comprise acids, esters and aldehydes in much lower concentrations (The Fischer Tropsch and Related Syntheses, H. H. Storch, N. Golumbic, R. B. Anderson, John Wiley & Sons, Inc., N.Y. 1951). It is generally known in the art that these oxygenated compounds are prevalently concentrated in the low-boiling fraction of a typical mixture obtained from the Fischer-Tropsch synthesis, whereas the fraction with a boiling point higher than 300°C, preferably higher than 370°C, has a content of organic oxygen not higher than 0.1% (expressed as weight of oxygen with respect to the total weight of the fraction).

In relation to the characteristics of the F.T. product, there are various kinds of hydrogenating treatment suitable for producing a hydrocarbon mixture which can be used as component (B). If the distillation range of the F.T. product is from 150 to 380°C, preferably from 240 to 370°C, the hydrogenating treatment is such as to hydrogenate the unsaturated and oxygenated groups, but not significantly reduce the average molecular weight. Experts in the field can decide whether to also apply a hydrogenating/isomerizing treatment according to what is known in the art, in order to give satisfactory low temperature properties, either as a subsequent step to the hydrogenation of the oxygenated groups, or contemporaneously with this in the presence of suitable hybrid catalysts, i.e. containing both hydrogenating functions (supported noble metals), and isomerizing functions (acid sites).

When, on the other hand, the F.T. product comprises significant parts of waxy high-boiling products, it is typically subjected to an upgrading process comprising one or more hydrocracking steps, optionally preceded by a hydrogenation step. As is known, a hydrocracking step is carried out in the presence of a bifunctional catalyst, containing a metal with a hydro-dehydrogenating activity supported on an inorganic solid comprising at least one oxide or silicate with acid characteristics.

Hydrocracking catalysts typically comprise metals of groups 6 to 10 of the periodic table of elements (in the form approved by IUPAC and published by "CRC Press Inc." in 1989, to which reference will be made hereunder), especially nickel, cobalt, molybdenum, tungsten or noble metals such as palladium or platinum. Whereas the former are more suitable for processing hydrocarbon mixtures with relatively high sulfur contents, noble metals are more active, but are poisoned by sulfur and other hetero-atoms and are therefore particularly suitable for processing hydrocarbon mixtures of the type obtained by means of F.T.

Carriers which can normally be used for the purpose are various types of zeolites (β, Y), X—Al, O₆ (wherein X can be Cl or F), silico-aluminas, the latter being amorphous or with varying degrees of crystallinity, or mixtures of crystalline zeolites and amorphous oxides. For greater details on the various catalysts, specific characteristics and different hydrocracking processes based thereon, reference should be made, among the numerous publications available in literature, to the publication of J. Scherzer and A. J. Gruia “Hydrocracking Science and Technology”, Marcel Dekker, Inc. Editor (1996).

In the upgrading treatment of products coming from the F.T. synthesis, it is preferable to precede the hydrocracking step by at least one hydrogenation step of the unsaturated and oxygenated compounds, especially alcohols, possibly present, as these can contribute to decreasing the activity of the hydrocracking catalyst and its lower stability with time. For example, patent application EP-A 321,303 (Shell) describes a process which comprises the separation of the light fraction (200-4°C, rich in oxygenated compounds) of a hydrocarbon mixture from an F.T. process, and sending the 290-4°C fraction to a hydrocracking/isomerization reactor for the production of medium distillates. The catalyst claimed for both reactors consists of platinum supported on fluorinated alumina.

European patent application EP-A 1101813 describes an upgrading process of a waxy F.T. product comprising a hydrogenating treatment step mainly aimed at removing the organic oxygen and unsaturations in the olefins and, if necessary, the partial isomerization of the lighter part of the product, typically carried out at a temperature ranging from 150 to 300°C, a hydrogen pressure ranging from 0.5 to 10 MPa and a space velocity (WHSV) ranging from 0.5 to 4 h⁻¹, with a hydrogen/filler ratio ranging from 200 to 2000 Nlt/Kg. The hydrogenation catalyst is based on nickel, platinum or palladium, supported on alumina, silico-alumina, fluorinated alumina, with a concentration of the metal which, depending on the type, ranges from 0.1 to 70%, preferably from 0.5 to 10%, by weight. The hydrogenated mixture is subsequently subjected to hydrocracking effected so as to provide a conversion degree of at least 50% and produce a medium distillate cut with high conversions and selectivities. The catalyst used for the purpose preferably consists of a noble metal, particularly Pt or Pd, supported on
an amorphous silica-alumina gel and micro/mesoporous with a controlled pore size, a surface area of at least 500 m²/g and a molar ratio SiO₂/Al₂O₃ ranging from 40/1 to 150/1, obtained according to one of the methods described in European patent applications EP-A 582,347, EP-A 701, 480 or EP 1,048,346, whose contents are incorporated herein as reference. At the end, the hydrocracking reaction mixture is sent to a distillation/selection step from which, operating according to the known art, a medium distillate is obtained, subdivided into gas oil and kerosene fractions, both suitable, but especially the gas oil fraction, as component (B) of the composition according to the present invention.

[0041] The F.T. hydrocarbon mixture which forms component (B) preferably comprises not less than 50%, more preferably from 60 to 90%, by weight of branched aliphatic hydrocarbons, of which at least 60% has a methyl branching, as determined with the gas-mass and NMR instrumental techniques currently available. Other preferred characteristics of this mixture are:

[0042] Cetane Number >60, more preferably >70

[0043] Pour Point <10°C, more preferably <25°C

[0044] Distillation range substantially overlapping (at least by ±20°C) that of component (A), more preferably from 240 to 370°C

[0045] The proportions of components (A) and (B) preferably range from 85 to 98% by weight and from 15 to 2% by weight respectively with respect to the overall weight of the two components. These together form from 80 to 100%, preferably from 90 to 100% by weight of the composition according to the present invention, the remainder optionally consisting of additives and smaller quantities of other components typically used in the preparation of fuels and combustibles according to the usual technique.

[0046] The composition according to the present invention can be easily prepared by mixing components (A) and (B) indicated above, in the suitable proportions. Any suitable method in the art can be adopted for the purpose, and there are no particular critical operating conditions. The composition can be obtained for example by batch mixing in suitable containers, or, more conveniently, in continuous, as normally happens within the scope of refinery processing. According to a possible but non-limiting embodiment, components (A) and (B), in appropriate proportions, are poured into a container and briefly mixed at room temperature until they are homogeneously dispersed in each other. The optional additives can be added, when desired, to the preformed mixture of (A) and (B), or they can be already present, in suitable quantities, in one or both of the components at the moment of mixing, preferably in component (A).

[0047] Particularly preferred, according to the present invention, are compositions in which the mixture of components (A) and (B) have a distillation range included in typical gas oil cuts, i.e. from 200°C to 380°C, more preferably from 240 to 360°C

[0048] Although the compositions according to the present invention show, as such, evident improvement in the lubricants properties, this does not exclude that they can also contain certain quantities of known additives for improving the lubricity. In this case, it has been found that the lubricating properties of the composition are however surprisingly improved with respect to a mixture consisting of component (A) alone with the same quantity of additive.

[0049] More generally, the compositions of the present invention can comprise up to 20%, preferably up to 10% by weight with respect to the total weight, of one or more additives usually used in the art for giving certain desired properties to compositions to be used as fuels, such as viscosity improvers, anti-freeze agents, additives for improving the combustion, such as cetane improvers and octave improvers.

[0050] In the preparation of the composition with an improved lubricating capacity of the present invention, these additives can be indifferentely added to the preformed mixture of components (A) and (B), or each additive can be independently added or contained in one of components (A) and (B), or again, said additives can be added, in any order, during and contemporaneously with the mixing of said components (A) and (B).

[0051] It has also been found that the lubricating capacity of a typically classifiable fuel such as a medium distillate can be surprisingly improved by the addition of relatively small quantities of non-oxygenated synthetic hydrocarbon cuts obtained from syntheses of the F.T. type.

[0052] A second object of the present invention therefore relates to a method for improving the lubricating capacity (lubricity) of a fuel for engines, characterized in that a synthetic hydrocarbon mixture essentially without oxygenated organic compounds, obtained by means of a process comprising a synthesis reaction of the Fischer-Tropsch type, having a distillation range comprised within 130 and 380°C, preferably within 150 and 370°C, more preferably within 240 and 370°C, is added to said fuel, in a quantity ranging from 1 to 25% by weight with respect to the fuel itself.

[0053] According to a preferred aspect, said fuel is particularly suitable for use in diesel engines and essentially has the characteristics of the refinery hydrocarbon mixture forming component (A) described above. The hydrocarbon mixture indicated above as preferred component (A), especially the component (A) defined as gas oil, suitable as a fuel for Diesel cycles, are therefore preferred as fuels suitable for effecting the method.

[0054] The above fuel can also contain, according to the present invention, one or more of the typical additives of fuels defined within the medium distillate range, as mentioned above. These additives do not generally exceed 20% by weight of the fuel.

[0055] It is also preferable, for the purposes of the present invention, for the method in question to comprise the addition and mixing with said fuel of a hydrocarbon mixture deriving from a Fischer-Tropsch synthesis, having a distillation range substantially overlapping that of the fuel.

[0056] Particularly advantageous results are obtained by adding to said fuel, a hydrocarbon mixture essentially having the characteristics previously specified for component (B) of the composition according to the present invention, more preferably in a quantity ranging from 2 to 15% by weight.
Some examples are provided for a more detailed description of the present invention and for its practical embodiment, which however merely illustrate particular aspects of the invention and should in no way be considered as limiting the overall scope of the invention itself.

EXAMPLES

The lubricating properties of the compositions described in the examples were evaluated by means of a lubricity measurement according to the HFRR (high frequency reciprocating rig) method. This method, developed at the Mechanical Engineering Department of London Imperial College has been recognized as being among the most qualified for the lubricating capacity or lubricity measurement of a composition suitable for use as a fuel, and is well known by experts in the field. The equipment for effecting this measurement is available on the market.

The equipment for effecting the measurement according to the HFRR method consists in an upper sphere loaded with a standard weight which oscillates against a lower static plate. The contact is totally immersed in the fuel on which the measurement is being effected. During the measurement, the friction and electric resistance of the contact are registered and the diameter of the wear trace on the sphere at the end of the test, is measured. In particular, a measuring instrument supplied by the company PCS Ltd. of London (UK) was used, with a load of 200 g on an AISI E-52100 steel sphere having a diameter of 6 mm, which oscillates on a plate made of the same material. The measurement is effected on a ml sample of fuel composition at 60° C.

In the following examples an essentially paraffinic hydrocarbon mixture was used, obtained by the hydrocracking and fractionation of a waxy mixture deriving from a traditional Fischer-Tropsch synthesis, according to the following method.

Preparative Example

A synthesis gas oil suitable as component (B) according to the present invention, was prepared, using a waxy product deriving from a Fischer-Tropsch process, essentially consisting of linear hydrocarbons according to the following composition (weight %):

<table>
<thead>
<tr>
<th>Fraction &lt;150° C.</th>
<th>4.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene (from 150 to 260° C.)</td>
<td>13.9</td>
</tr>
<tr>
<td>Gas oil (from 260 to 370° C.)</td>
<td>55.4</td>
</tr>
<tr>
<td>Alcohol (weight %)</td>
<td>4.7</td>
</tr>
</tbody>
</table>

This mixture was subjected to hydrocracking treatment according to the known techniques, and particularly according to what is described in Example 5 of the patent EP-A 1101813.

At the end, after fractionation, a fraction was obtained within the distillation range of gas oil (Gas oil FT, yield 46%) having the following characteristics:

<table>
<thead>
<tr>
<th>HFRR (wear diameter, (um))</th>
<th>607</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content of sulfur and aromatics</td>
<td>absent</td>
</tr>
<tr>
<td>Density</td>
<td>0.824 Kg/dm³</td>
</tr>
<tr>
<td>Distillation range</td>
<td>250–360° C</td>
</tr>
<tr>
<td>Oxygen content</td>
<td>less than 0.001 wt %</td>
</tr>
</tbody>
</table>

This fraction was used without further modifications or additives in the following examples.

Example 1

Three hydrocarbon compositions with an improved lubricity according to the present invention, were prepared, to be used as fuel for diesel engines, by mixing different proportions of the following two components:

A) A refinery gas oil cut called “Gas oil A”, having the following characteristics:

<table>
<thead>
<tr>
<th>HFRR, wear diameter (um)</th>
<th>407</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur (weight %)</td>
<td>0.8</td>
</tr>
<tr>
<td>Density at 15° C.</td>
<td>0.8491</td>
</tr>
<tr>
<td>Aromatics (weight %)</td>
<td>25.2</td>
</tr>
<tr>
<td>Distillation range (° C.)</td>
<td>230–570</td>
</tr>
</tbody>
</table>

B) an essentially paraffinic hydrocarbon mixture consisting of “Gas oil FT” obtained according to the above Preparative Example.

Some of the properties of the compositions thus obtained, indicated as (i), (ii) and (iii) respectively, are indicated in Table 1 below, together with the relative proportions of components (A) and (B).

Example 2

Four hydrocarbon compositions with an improved lubricity according to the present invention, were prepared, to be used as fuel for diesel engines, by mixing different proportions of the following two components:

A) A refinery gas oil cut called “Gas oil B”, having the following characteristics:

<table>
<thead>
<tr>
<th>HFRR, wear diameter (um)</th>
<th>505</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur (weight %)</td>
<td>0.023</td>
</tr>
<tr>
<td>Density at 15° C.</td>
<td>0.8429</td>
</tr>
<tr>
<td>Aromatics (weight %)</td>
<td>30.4</td>
</tr>
<tr>
<td>Distillation range (° C.)</td>
<td>230–370</td>
</tr>
</tbody>
</table>

B) an paraffinic hydrocarbon mixture consisting of “Gas oil FT” obtained as described above.

Some of the properties of the compositions thus obtained, indicated as (i), (ii), (iii) and (iv) respectively, are indicated in Table 1 below, together with the relative proportions of components (A) and (B).

Example 3

Three hydrocarbon compositions with an improved lubricity according to the present invention, were prepared,
to be used as fuel for diesel engines, by mixing different proportions of the following two components:

A) a refinery gas oil cut called “Gas oil C”, having the following characteristics:

<table>
<thead>
<tr>
<th>HFRR, wear diameter (µm)</th>
<th>675</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfur (weight %)</td>
<td>0.0047</td>
</tr>
<tr>
<td>density at 15 °C</td>
<td>0.7971</td>
</tr>
<tr>
<td>aromatics (weight %)</td>
<td>8.8</td>
</tr>
<tr>
<td>distillation range (°C)</td>
<td>230–310</td>
</tr>
</tbody>
</table>

B) an paraffinic hydrocarbon mixture consisting of “Gas oil FT” obtained as described above.

Some of the properties of the compositions thus obtained, indicated as (i), (ii) and (iii) respectively, are indicated in Table 1 below, together with the relative proportions of components (A) and (B).

As can be seen from Table 1 below, the compositions according to the present invention all have a surprisingly improved lubricity (lower HFRR wear diameter values) with respect to the lubricity of both of the original components A and B. In the case represented by Example 2, the improvement in lubricity is such as to allow specification values to be reached (HFRR 2<450 µm) even though both of the original components have higher HFRR values (505 µm and 607 µm respectively).

| TABLE 1 |
|------------------|------------------|
|                  | Example 1         | Example 2         |
| “Gasoil A” (wt %)| “Gasoil FT” (wt %)| “Gasoil A” (wt %)| “Gasoil FT” (wt %)| “Gasoil A” (wt %)| “Gasoil FT” (wt %) |
| Refinery gas oil alone | 100 | 0 | 407 | 100 | 0 | 505 |
| (i)               | 95  | 5 | 360 | 98  | 2 | 436 |
| (ii)              | 90  | 10| 330 | 90  | 10| 444 |
| (iii)             | 80  | 20| 330 | 85  | 15| 457 |
| (iv)              | —   |   | —  80| 20  |   | 466 |

1. Hydrocarbon compositions, to be used as fuel for diesel or turbine engines, wherein at least 80% by weight has a distillation range comprised within 150 and 380° C., and consists of a mixture of the following components:

(A) from 80 to 99% by weight with respect to the overall weight of (A) and (B) of any refinery hydrocarbon mixture, having a distillation range comprised within 150 and 380° C.,

(B) from 1 to 20% by weight with respect to the overall weight of (A) and (B) of a hydrocarbon mixture essentially without oxygenated organic compounds, obtained by means of a process comprising a synthesis reaction of the Fischer-Tropsch type, having a distillation range comprised within 130 and 380° C.

2. The composition according to the previous claim 1, consisting of from 90% to 100% by weight of said components (A) and (B), jointly.

3. The composition according to any of the claims 1 or 2, wherein said components (A) and (B), jointly have a distillation range comprised within 200 and 380° C.

4. The composition according to any of the previous claims, wherein the proportions of said components (A) and (B) respectively range from 85 to 98% by weight and from 15 to 2% by weight with respect to the over-all weight of (A) and (B).

5. The composition according to any of the previous claims, wherein said component (A) is a hydrocarbon mixture having a distillation range comprised within 200 and 370° C.

6. The composition according to claim 5, wherein said component (A) essentially consists of a non-synthetic gas oil fraction with a distillation range comprised within 240 and 360° C.

7. The composition according to any of the previous claims, wherein said component (A) has a sulfur content lower than 1000 ppm as S weight.

8. The composition according to any of the previous claims, wherein said component (B) was obtained by a process comprising at least one hydrocracking step.

9. The composition according to any of the previous claims, wherein at least 50% of said component (B) consists of branched paraffins.

10. The composition according to any of the previous claims, wherein said component (A) and said component (B) have essentially overlapping distillation ranges.

11. The composition according to any of the previous claims, wherein said component (B) has the following characteristics:

- Cetane Number >60
- Pour Point <-10° C.
- Distillation range from 240 to 370° C.

12. The composition according to any of the previous claims, comprising, in addition to said components (A) and (B), up to 20%, preferably up to 10% by weight with respect to the total weight, of one or more additives for fuel products.

13. Use as engine fuel of the composition according to any of the previous claims from 1 to 12.

14. Use according to claim 13, as fuel for feeding Diesel engines.

15. A method for improving the lubricating properties of an engine fuel, characterized in that a synthetic hydrocarbon mixture essentially without organic oxygenated compounds,
obtained by a process comprising a synthesis reaction of the Fischer-Tropsch type, having a distillation range comprised within 130 and 380° C., preferably within 150 and 370° C., is added to said fuel, in a quantity ranging from 1 to 25% by weight with respect to the fuel itself.

16. The method according to claim 15, wherein said fuel consists of a refinery hydrocarbon mixture, having a distillation range comprised within 150 and 380° C.

17. The method according to any of the previous claims from 15 to 16, wherein synthetic mixture is added in a quantity ranging from 2 to 15% by weight with respect to said fuel.

18. The method according to any of the previous claims from 15 to 17, wherein said fuel is a refinery hydrocarbon mixture having a distillation range comprised within 200 and 370° C.

19. The method according to any of the previous claims from 15 to 18, wherein said fuel has a sulfur content lower than 1000 ppm as S weight.

20. The method according to any of the previous claims from 15 to 19, wherein synthetic mixture was obtained by means of a process comprising at least one hydrocracking step.

21. The method according to any of the previous claims from 15 to 20, wherein said fuel and said synthetic mixture have essentially overlapping distillation ranges.

22. The method according to any of the previous claims from 15 to 21, wherein said synthetic mixture has the following characteristics:

Cetane Number >60

Pour Point <=-10° C.

Distillation range comprised within 240 and 370° C.

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