ABSTRACT

A process to blend a mineral derived hydrocarbon product and a Fischer-Tropsch derived hydrocarbon product is disclosed including the step of providing in an Above Ground Storage Tank a quantity of mineral derived hydrocarbon product and Fischer-Tropsch derived hydrocarbon product such that initially the mineral derived hydrocarbon product is located substantially above the Fischer-Tropsch derived hydrocarbon product.
PROCESS TO BLEND A MINERAL DERIVED HYDROCARBON PRODUCT AND A FISCHER-TROPSCH DERIVED HYDROCARBON PRODUCT

FIELD OF THE INVENTION

[0001] The present invention relates to a process to blend a mineral derived hydrocarbon product and a Fischer-Tropsch derived hydrocarbon product.

BACKGROUND OF THE INVENTION

[0002] A process to blend mineral derived gas oil and a Fischer-Tropsch derived gas oil is described in WO-A-03/087273. This publication describes that a mineral derived gas oil may be blended in a refinery environment to achieve a blended product having a certain cetane number.

[0003] Although WO-A-03/087273 provides a process to achieve a blend having a certain quality property it can still be improved in terms of the blending operation itself.

SUMMARY OF THE INVENTION

[0004] A process to blend a mineral derived hydrocarbon product and a Fischer-Tropsch derived hydrocarbon product is provided comprising the steps of: providing in an Above Ground Storage Tank a quantity of mineral derived hydrocarbon product and Fischer-Tropsch derived hydrocarbon product such that initially the mineral derived hydrocarbon product is located substantially above the Fischer-Tropsch derived hydrocarbon product.

DETAILED DESCRIPTION OF THE INVENTION

[0005] Applicants found that a fully blended product can be obtained by the process according to the invention. The following process makes available a blended product suited for direct use at for example a refinery environment.

[0006] Thus, in accordance with the present invention there is provided a process to blend a mineral derived hydrocarbon product and a Fischer-Tropsch derived hydrocarbon product by providing in an Above Ground Storage Tank a quantity of mineral derived hydrocarbon product and Fischer-Tropsch derived hydrocarbon product such that initially the mineral derived hydrocarbon product is located substantially above the Fischer-Tropsch derived hydrocarbon product.

[0007] The Fischer-Tropsch derived hydrocarbon product is suitably obtained by converting a mixture of carbon monoxide and hydrogen in the presence of a suitable Fischer-Tropsch catalyst under Fischer-Tropsch operating conditions. The catalysts used for the catalytic conversion of the mixture comprising hydrogen and carbon monoxide into the Fischer-Tropsch derived paraffinic hydrocarbon product are known in the art. Catalysts for use in this process frequently comprise, as the catalytically active component, a metal from Group VIII of the Periodic Table of Elements. Particular catalytically active metals include ruthenium, iron, cobalt and nickel. Cobalt is a preferred catalytically active metal.


[0009] Syngas, i.e. the mixture of carbon monoxide and hydrogen used in the Fischer-Tropsch process, may be prepared from various hydrocarboneous sources such as for example biomass, coal, mineral crude oil fractions like residual fractions and methane containing gases, for example natural gas or coal bed methane gas.

[0010] The Fischer-Tropsch derived hydrocarbon product is suitably liquid at 0°C. If the product is not liquid it is preferably kept in the Above Ground Storage Tank at conditions at which the product is liquid. The Fischer-Tropsch derived product can be the wax as is directly prepared in the Fischer-Tropsch synthesis step. Suitably this Fischer-Tropsch synthesis product is first subjected to a mild hydrosisomeration to reduce the coagulating point of the product and increase its pumpability and to more easily have the product in the liquid state in the process of the present invention. Such a product is also referred to as Synercorde.

[0011] The Fischer-Tropsch derived hydrocarbon product may also be the lower boiling liquid fractions as isolated from the waxy Fischer-Tropsch product boiling between 35 and 300°C. These products comprising substantially, i.e. more than 80 wt%, of normal paraffins, may be shipped as hydrocarbon solvents, as steam cracker feedstock or as feedstock for the preparation of detergents.

[0012] Alternatively the waxy product is subjected to a hydrocracking/hydrosisomeration process wherein lower boiling fractions are obtained, such as for example paraffin products boiling in the naphtha, kerosene and gas oil boiling range. The partly isomerised liquid products so obtained may be shipped to end customers for use as aviation fuel, diesel fuel, industrial gas oil, drilling fluids, steam cracker feedstock or solvents. The partly isomerised wax, also referred to as waxy raffinate, as obtained in such processes, may advantageously be further processed by means of solvent or catalytic dewaxing to obtain lubricating base oils or may be shipped as such to be used as an intermediate product to base oil manufacturing locations nearer to the end users. Waxy raffinate is a distillate fraction. Residual fractions boiling in the base oil range may also be used. However, it may be more difficult to keep these products in a liquid state during blending. Examples of such processes are described in more detail in U.S. Pat. Nos. 6,309,432, 6,296,757, 5,689,031, EP-A-0668342, EP-A-0583836, U.S. Pat. No. 6,420,618, WO-A-02/070629, WO-A-02/070627, WO-A-02/064710 and WO-A-02/070630. The referred to hydrocracking/hydrosisomeration and optimal dewaxing steps are thus performed at the Fischer-Tropsch manufacturing location and the resulting above described liquid products are suitably used as the Fischer-Tropsch hydrocarbon products to be shipped.

[0013] The volume ratio between the mineral derived hydrocarbon product and the Fischer-Tropsch derived product may range, for example, from 1:99 to 99:1 and more preferably from 10:90 to 90:10. The mineral derived hydrocarbon product preferably has a T90 vol % boiling point, as measured by ASTM D86, which is greater than the T50 vol
% boiling point of the Fischer-Tropsch derived hydrocarbon product. More preferably, more than 50 vol %, and even more preferably more than 80 vol %, of the boiling ranges of the mineral and the Fischer-Tropsch derived products overlap.

[0014] The mineral hydrocarbon product may be any product which is extracted from a subterranean environment or derivatives therefrom. Examples of such products are crude mineral oil, gas field condensates, plant condensates, naphtha, kerosene, gas oil, vacuum distillates, deasphalted oils and residual fractions of crude oils.

[0015] Examples of combinations for which the present process will find utility are the blending of mineral crude oil and syncrude, blending of Fischer-Tropsch derived naphtha and gas field condensate, blending of Fischer-Tropsch derived gas oil and mineral derived gas oil and the blending of Fischer-Tropsch derived waxy raffinate and mineral oil derived vacuum distillates and/or mineral oil derived deasphalted oil.


[0017] Suitable the Fischer-Tropsch derived gas oil will consist at least 90 wt %, preferably at least 95 wt % of iso and linear paraffins. The weight ratio of iso-paraffins to normal paraffins suitably be greater than 0.3. This ratio may be up to 12. Suitably this ratio is from 2 to 6. The actual value for this ratio will be determined, in part, by the hydroconversion process used to prepare the Fischer-Tropsch derived gas oil from the Fischer-Tropsch synthesis product. Some cyclic-paraffins may be present. By virtue of the Fischer-Tropsch process, the Fischer-Tropsch derived gas oil has essentially zero content of sulphur and nitrogen (or amounts which are no longer detectable). These heteroatom compounds are poisons for Fischer-Tropsch catalysts and are removed from the synthesis gas that is the feed for the Fischer-Tropsch process. Further, the process does not make aromatics, or, as usually operated, virtually no aromatics are produced. The content of aromatics as determined by ASTM D 4629 will typically be below 1 wt %, preferably below 0.5 wt % and most preferably below 0.1 wt %.

[0018] The Fischer-Tropsch derived gas oil will suitably have a distillation curve which will for its majority be within the typical gas oil range: from 150 to 400°C. The Fischer-Tropsch gas oil will suitably have a T90 wt % of from 320 to 400°C, a density of from 0.76 to 0.79 g/cm³ at 15°C, a cetane number greater than 70, suitably from 74 to 82, and a viscosity of from 1.9 to 4.5 centistokes at 40°C.

[0019] The above Fischer-Tropsch derived gas oil is preferably blended with a mineral derived kerosene or gas oil or mixtures of said kerosene and gas oil. Preferred mineral derived gas oils or kerosenes are gas oils or kerosenes as obtained from refining and optionally (hydro)processing of a crude mineral source or the gas oil or kerosene fraction as isolated from a gas field condensate. The mineral derived gas oil may be a single gas oil stream as obtained in such a refinery process or be a blend of several gas oil fractions obtained in the refinery process via different processing routes. Examples of such different gas oil fractions as produced in a refinery are straight-run gas oil, vacuum gas oil, gas oil as obtained in a thermal cracking process and light and heavy cycle oil as obtained in a fluid catalytic cracking unit and gas oil as obtained from a hydrocracker or the equivalent kerosene fraction.

[0020] The straight run gas oil or kerosene fraction is the fraction which has been obtained in the atmospheric distillation of the crude mineral refinery feedstock. The above fractions suitably have an Initial Boiling Point (IBP) of from 150 to 280°C and a Final Boiling Point (FBP) of from 290 to 380°C. The vacuum gas oil is the gas oil fraction as obtained in the vacuum distillation of the residue as obtained in the above referred to atmospheric distillation of the crude mineral refinery feedstock. The vacuum gas oil has an IBP of from 240 to 300°C and a FBP of from 340 to 380°C. The thermal cracking process also produces a gas oil fraction, which may be used in step (a). This gas oil fraction has an IBP of from 180 to 280°C and a FBP of from 320 to 380°C. The light cycle oil fraction as obtained in a fluid catalytic cracking process will have an IBP of from 180 to 260°C and a FBP of from 320 to 380°C. The heavy cycle oil fraction as obtained in a fluid catalytic cracking process will have an IBP of from 240 to 280°C and a FBP of from 340 to 380°C. These feedstocks may have a sulphur content of above 0.05 wt %. The maximum sulphur content will be about 2 wt %. Although the Fischer-Tropsch derived gas oil comprises almost no sulphur it could still be necessary to lower the sulphur level of the mineral derived gas oil in order to meet the current stringent low sulphur specifications. Typically the reduction of sulphur will be performed by processing these gas oil fractions in a hydrodesulphurisation (HDS) unit.

[0021] Gas oil as obtained in a fuels hydrocracker has suitably an IBP of from 150 to 280°C and a FBP of from 320 to 380°C.

[0022] The cetane number of the blend of mineral derived gas oil as described above is preferably greater than 40 and less than 70. If also other properties like, for example, cloud point, CFPP (cold filter plugging point), flash point, density, di-aromatics content, polyaromatics and/or distillation temperature for 95% recovery comply with the local regulations, the blend may be advantageously used as a diesel fuel component.

[0023] Preferably the final blended gas oil product comprising the Fischer-Tropsch and the mineral derived gas oil will have a sulphur content of at most 2000 ppmw (parts per million by weight) sulphur, preferably no more than 500 ppmw, most preferably no more than 50 or even 10 ppmw. The density of such a blend is typically less than 0.86 g/cm³ at 15°C, and preferably less than 0.845 g/cm³ at 15°C. The lower density of such a blend as compared to conventional gas oil blends results from the relatively low density of the Fischer-Tropsch derived gas oils. The above fuel composi-
tion is suited as fuel in an indirect injection diesel engine or a direct injection diesel engine, for example of the rotary pump, in-line pump, unit pump, electronic unit injector or common rail type.

[0024] The final gas oil blend may be an additised (additive-containing) oil or an unadditised (additive-free) oil. If the fuel oil is an additised oil, it will contain minor amounts of one or more additives.

[0025] Detergent-containing fuel additives are known and commercially available. Such additives may be added to fuels at levels intended to reduce, remove or show the build up of engine deposits. Examples of detergents suitable for use in fuel additives for the present purpose include polyolefin substituted succinimides or succinimides of polyamines, for instance polysobutylene succinimides or polysobutylene amine succinimides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0174240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808, the disclosures are hereby incorporated by reference. Particularly preferred are polyolefin substituted succinimides such as polysobutylene succinimides.

[0026] Other additive components include lubricity enhancers, including ester- and acid-based additives; dehazers, e.g. alkoxylated phenol formaldehyde polymers; anti-foaming agents (e.g. polyether-modified polyols); ignition improvers ( cetane improvers) (e.g. 2-ethylhexyl nitrate (EHN), cyclohexyl nitrate, di-tert-butyl peroxide and those disclosed in U.S. Pat. No. 4,208,190 at column 2, line 27 to column 3, line 21); anti-rust agents (e.g. a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polysobutylene-substituted succinic acid); corrosion inhibitors; reodorants; anti-wear additives; anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N-di-sec-butyl-p-phenylenediamine); metal deactivators; and combustion improvers.

[0027] The additive concentration of each such additional component in the additivated fuel composition is preferably up to 1% w/w, more preferably in the range from 5 to 1000 ppmw, advantageously from 75 to 300 ppmw, such as from 95 to 150 ppmw.

[0028] In addition to the above gas oil components also a relatively small portion of an oxygenate type fuel component may be present in the final blend to obtain diesel fuel as for example described in WO-A-2004/035713. The oxygenate fuel may be present in a content of from 2 to 20 wt %, more preferably from 2 to 10 wt % as measured in the final fuel composition. The oxygenate is an oxygen containing compound, preferably containing only carbon, hydrogen and oxygen. It may suitably be a compound containing one or more hydroxyl groups —OH, and/or one or more carboxyl groups —COOH, and/or one or more other groups —O—, and/or one or more ester groups —C(O)O—. It preferably contains from 1 to 18 carbon atoms and in certain cases from 1 to 10 carbon atoms. Ideally it is biodegradable. It is suitably derived from organic material, as in the case of currently available “biofuels” such as vegetable oils and their derivatives.

[0029] Preferred oxygenates for use are esters, for example alkyl, preferably C₁ to C₂₄ or C₁ to C₆, such as methyl or ethyl, esters of carboxylic acids of vegetable oils. The carboxylic acid in this may be an optionally substituted, straight or branched chain, mono-, di- or multifunctional C₁ to C₆ carboxylic acid, typical substituents including hydroxy, carboxyl, ether and ester groups. Suitable examples of oxygenates (iii) include succinates and levulinates.

[0030] Ethers are also usable as the oxygenate (iii), for example dialky1 (typically C₁₂ to C₂₀) ethers such as dibutyl ether and dimethyl ether.

[0031] Alternatively the oxygenate may be an alcohol, which may be primary, secondary or tertiary. It may in particular be an optionally substituted (though preferably unsubstituted) straight or branched chain C₁ to C₂₀ alcohol, suitable examples being methanol, ethanol, n-propanol and iso-propanol. Typical substituents include carbonyl, ether and ester groups. Methanol and in particular ethanol may for instance be used.

[0032] The oxygenate (iii) will typically be a liquid at ambient temperature, with a boiling point preferably from 100 to 360°C, more preferably from 250 to 290°C. Its density is suitably from 0.75 to 1.2 g/cm³, more preferably from 0.75 to 0.9 g/cm³ at 15°C (ASTM D4502/IP 365), and its flash point greater than 55°C.

[0033] Adding the additives and/or the oxygenates may be performed during the process of the present invention. Even more preferably is to add at least part of the additives and/or the oxygenates when discharging the blended product from the storage vessel. Addition is preferably performed by means of so-called in-line blending. This is advantageous because the blend as thus obtained can be directly used as a finished fuel for use as Automotive Gas Oil (AGO) or as an Industrial Gas Oil (IGO).

[0034] By “substantially above” in the sense of the process of the present invention is meant that at least 50, preferably at least 70 and even more preferably at least 90 vol %, of the Fischer-Tropsch derived product is present in the lower half of the Above Ground Storage Tank. When loading the Above Ground Storage Tank using a bottom filling device the mineral hydrocarbon product is preferably supplied first and the Fischer-Tropsch derived product second.

[0035] By a “blended product” is meant a mixture wherein the difference in density between a sample taken at 10% of the liquid height below the liquid surface, referred to as d10, and the density of a sample taken at 90% of the liquid height below the liquid surface, referred to as d90, is small, preferably such that the ratio of the (d10/d90) is less than 0.01, more preferably less than 0.001.

[0036] The “Above Ground Storage Tank” also referred to as a “AST” in the sense of the present invention is a storage facility fixed to the surface of the earth. Preferably the Above Ground Storage Tank is part of a so-called blending facility or tanker park. The Above Ground Storage Tank has suitably a storage volume of greater than 3000 m³, more preferably greater than 10000 m³. The upper limit of the
storage facility of a single Above Ground Storage Tank is suitably 100,000 m$^3$. The Above Ground Storage Tank may be equipped with additional mixing devices as may be present in Above Ground Storage Tanks. An advantage of the process of the present invention is that such devices may be omitted or used at a lower rate.

0037 The present invention is also directed to a blended product produced by the process to blend according to the present invention.

0038 The present invention is further directed to the direct use of the blended product as a fuel, more preferably as an automotive gas oil or as an industrial gas oil, as obtained by the process of the present invention.

0039 The present invention will be illustrated by means of the following non-limiting examples.

\textbf{EXAMPLE}

\textbf{0040} A typical mineral derived gas oil (further referred to as AGO) and a typical Fischer-Tropsch gas oil (further referred to as GTL) having the properties as listed in Table 1 were used in the following experiment.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
Fuel Reference & Units & AGO & GTL \\
\hline
Cetane Index (ASTM D6613) & 51.5 & >74.8 \\
Sulphur mg/kg & 7 & <5 \\
V$k_{10}$ & 211 & 2.559 & 3.606 \\
Distillation & & & \\
IBP & °C. & 167.8 & 211 \\
50% & °C. & 263.5 & 298 \\
90% & °C. & 325.3 & 399 \\
95% & °C. & 341.6 & 349 \\
FBP & °C. & 381.2 & 354 \\
HPLC Aromatics & wt % & 26.9 & 0 \\
\hline
\end{tabular}
\caption{Table 1}
\end{table}

0041 Two methods of fuel addition were adopted for this assessment, although the essence of both experiments remained the same. These methods were the Funnel Technique and the Beaker Technique.

0042 The objective of each technique was to minimise turbulence (and hence mixing) during addition of the second fuel so that the majority of any mixing of the two fuels was due to the length of the contact time. Both techniques involved the preparation of 2×2 litre glass beakers, one containing 800 ml of AGO, the other containing 800 ml of GTL. To the AGO, 800 ml of GTL was added slowly, using a 1 litre glass cylinder, taking approximately 2 minutes to complete (Blend A). This technique was repeated for the addition of the AGO (800 ml) to GTL (Blend B). To evaluate blend homogeneity, densities of the fuel blends were measured after a period of time at 400 ml and 1200 ml from the bottom of the beaker to assess the density at bottom and top of each blend. The funnel technique for fuel addition involved the pouring of the added fuel over the outer surface of an upside down glass funnel that had its base (funnel mouth) in contact with the inner walls of the glass beaker. This was designed to produce fuel addition over a large surface area, minimise turbulence and hence minimise the mixing of the two fuel layers during addition of the second fuel.

0043 The beaker technique for fuel addition involved the direct pouring of the added fuel down the inner wall of the beaker. This produced fuel addition over a smaller surface area than that of the funnel technique, more turbulence and hence more mixing of the two fuel layers during addition of the second fuel.

0044 Density follows, volume/volume, linear blending rules and a homogeneous 50:50 blend of the AGO and GTL samples studied will have a theoretical density of 813.3 kg/m$^3$. Thus, density measurements of the blends can be used to calculate the amount of each component present.

0045 Table 2 depicts the density results and calculated percentage for each component sampled at a depth represented by a volume of 400 ml (bottom), and 1200 ml (top) on the graduated beaker. It should be noted that the density result of 841.8 kg/m$^3$ obtained for Blend A ‘Bottom’—funnel method, is greater than 841.4 kg/m$^3$—the density of neat AGO. However, this result does fall within the reproducibility of the IP365 method, and the result indicates that the ‘Bottom’ sample is 100% AGO.

0046 The times that the blends were sub sampled for density analysis were not considered to have to be identical, as the appearance of each blend did not seem to change over the 24-hour period observed.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Method type & Blend ref. & Blend configuration & Time at which the blend was checked (minutes) & Density of layer (kg/m$^3$) & Fischer-Tropsch derived gas oil wt vol % \\
\hline
Funnel & A & GTL on top, AGO on bottom & 135 & 781.8 & 94 & 6 \\
method & & & & 841.8 & 0 & 100 \\
Beaker & method & GTL on top, AGO on bottom & 10 & 797.7 & 78 & 22 \\
method & & & & 824.3 & 30 & 70 \\
Funnel & B & AGO on top, GTL on bottom & 145 & 810.9 & 55 & 45 \\
method & & & & 815.8 & 46 & 54 \\
Beaker & method & AGO on top, GTL on bottom & 7 & 810.0 & 56 & 44 \\
method & & & & 816.5 & 44 & 56 \\
\hline
\end{tabular}
\caption{Table 2}
\end{table}

0047 When considering respective sets of blends A and B for each method, it is obvious by the percentage of each component present, at both top and bottom, of each blend that to provide optimum blending without agitation then the AGO should be added on top of the GTL and not vice versa.

1. A process to blend a mineral derived hydrocarbon product and a Fischer-Tropsch derived hydrocarbon product comprising the steps of: providing in an Above Ground Storage Tank a quantity of mineral derived hydrocarbon product and Fischer-Tropsch derived hydrocarbon product such that initially the mineral derived hydrocarbon product is located substantially above the Fischer-Tropsch derived hydrocarbon product.

2. The process of claim 1 wherein initially at least 50 vol % of the Fischer-Tropsch derived product is present in the lower half of the Above Ground Storage Tank.
3. The process of claim 1 wherein more than 50% of the boiling ranges of the mineral and the Fischer-Tropsch derived products overlap.

4. The process of claim 2 wherein more than 50% of the boiling ranges of the mineral and the Fischer-Tropsch derived products overlap.

5. A process of claim 1 wherein the mineral hydrocarbon product comprises a crude mineral oil, a gas field condensate, a plant condensate or naphtha, kerosene, gas oil, vacuum distillate, deasphalted oil or residual fraction of crude oils.

6. The process of claim 5 wherein the blended product is a blend of a mineral crude oil and Fischer-Tropsch syncrude, a blend of Fischer-Tropsch derived naphtha and gas field condensate, a blend of Fischer-Tropsch derived gas oil and mineral derived gas oil or a blend of a Fischer-Tropsch derived waxy raffinate and mineral oil derived vacuum distillate and/or mineral oil derived deasphalted oil.

7. A process of claim 6 wherein a blend of Fischer-Tropsch derived gas oil and mineral derived gas oil is prepared.

8. The process of claim 7 wherein to the blend additives are added while emptying the blended product from the Above Ground Storage Tank.

9. A blended product produced by the process of claim 1.

10. A blended product produced by the process of claim 9.