ABSTRACT

A process for hydrogenating a low sulphur blended feed into very low sulphur and very low aromatic hydrocarbon fluids having a boiling point in the range of from 100 to 400°C and a boiling range of not more than 80°C, the low-sulphur blended feed including a mixture of:

i) a hydrocarbon cut originating from a gas-to-liquid process with

ii) at least one selected from the group consisting of a hydrodeoxygenated hydrocarbon cut obtained from biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof;

the process including the step of catalytically hydrogenating the feed at a temperature from 80 to 180°C and at a pressure from 50 to 160 bars.
PROCESS FOR THE PRODUCTION OF HYDROCARBON FLUIDS HAVING A LOW AROMATIC AND SULFUR CONTENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a National Phase Entry of International Patent Application No. PCT/EP2014/073894, filed on Nov. 6, 2014, which claims priority to French Patent Application Serial No. 1361250, filed on Nov. 18, 2013, both of which are incorporated by reference herein.

TECHNICAL FIELD

[0002] The invention relates to the production of hydrocarbon fluids, called hereinafter specific fluids, having a narrow boiling range and having a very low aromatic content and their uses. The invention relates to hydrogenation conditions of Gas to Liquid (GTL)-derived feedstock in blend for the production of the specific fluids.

BACKGROUND

[0003] Hydrocarbon fluids find widespread use as solvents such as in adhesives, cleaning fluids, explosives solvents, for decorative coatings and printing inks, light oils for use in applications such as metal extraction, metalworking or demoulding and industrial lubricants, and drilling fluids. The hydrocarbon fluids can also be used as extender oils in adhesives and sealant systems such as silicone sealants and as viscosity depressants in plasticised polyvinyl chloride formulations and as carrier in polymer formulation used as flocculants for example in water treatment, mining operations or paper manufacturing and also used as thickener for printing pastes. Hydrocarbon fluids may also be used as solvents in a wide variety of other applications such as chemical reactions.

[0004] The chemical nature and composition of hydrocarbon fluids varies considerably according to the use to which the fluid is to be put. Important properties of hydrocarbon fluids are the distillation range generally determined by ASTM D-86 or the ASTM D-1160 vacuum distillation technique used for heavier materials, flash point, density, aniline point as determined by ASTM D-611, aromatic content, sulphur content, viscosity, colour and refractive index. Fluids can be classified as paraffinic, isoparaffinic, deaeromatised, naphthenic, non-deaeromatised and aromatic.

[0005] These fluids tend to have narrow boiling point ranges as indicated by a narrow range between Initial Boiling Point (IBP) and Final Boiling Point (FBP) according to ASTM D-86. The Initial Boiling Point and the Final Boiling Point will be chosen according to the use to which the fluid is to be put. However, the use of the narrow cuts provides the benefit of a narrow flash point which is important for safety reasons. The narrow cut also brings important fluid properties such as a better defined aniline point or solvency power, then viscosity, and defined evaporation conditions for systems where drying is important, and finally better defined surface tension.

[0006] To produce these specific fluids, the preferred feedstocks are specific gasoil cuts, such as low sulphur feed. A typical feed could be hydrocracked vacuum gas oil (VGO) for example.

[0007] Classical feeds produced in refineries cannot be used because of their high sulphur and aromatic contents. They are too heavy, besides their relative high density is commercially unfavourable. Moreover, sulphur is a poison for the deaeromatisation catalyst and aromatics compounds have to be hydrogenated in order to obtain high purity products. If the initial aromatic content of the feed is too high or if the molecules are resistant, the deaeromatisation step will be difficult to conduct and the final products will have non-relevant technical specifications. It is thus impossible to use a classical gasoil feed produced in refineries although it is broadly available in comparison with specific gas oils.

[0008] One aim of the invention is to provide a process for preparing specific fluids, which process does not require using hydrocracked vacuum gas oil (HCVGO) as a feed. Another aim of the invention is to provide a process which uses a lower amount of hydrocracked vacuum gas oil in the feed.

[0009] Another aim of the invention is to find a hydrogenation process with improved efficiency. Improved efficiency means that for a given content of aromatics in the feedstock, the content of aromatics in the hydrogenated product is lower than that obtained in the hydrogenated products produced by the hydrogenation processes of the prior art. In particular, the aim of the invention is to find a process exhibiting an improved efficiency with respect to the reduction of the monoaaromatics content. Another aim of the invention is to find a hydrogenation process, in which the hydrogenation catalyst is less sensitive to deactivation.

SUMMARY

[0010] The invention provides a process for hydrogenating a low-sulphur blended feed into very low sulphur and very low aromatic hydrocarbon fluids having a boiling point in the range of from 100 to 400°C, and a boiling range of not more than 80°C.

[0011] said low-sulphur blended feed comprising a mixture of:

[0012] i) a hydrocarbon cut originating from a gas-to-liquid process with

[0013] ii) at least one selected from the group consisting of a hydrodeoxygenated hydrocarbon cut obtained from biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof;

[0014] said process comprising the step of catalytically hydrogenating said feed at a temperature from 80 to 180°C, and at a pressure from 50 to 160 bars.

[0015] Surprisingly the applicant has found that classical gasoil feeds produced in refineries can be processed and used to produce specific fluids by blending them with hydrocarbon cuts originating from a gas-to-liquid process. The Applicant has also surprisingly found that when the blended feed is used in the hydrogenation process, then the aromatics content in the hydrogenated hydrocarbon fluid, especially the monoaaromatics content, is lower than that which is obtained when the feed is devoid of a hydrocarbon cut originating from a gas-to-liquid process; the aromatics content in the blended feed before hydrogenation being the same as that of the feed devoid of a hydrocarbon cut originating from a gas-to-liquid process. Using the blended feed according to the invention allows reducing the aromatics content in the hydrogenated hydrocarbon fluid. Further, the Applicant has found that using the blended feed in the hydrogenation process allows reducing the catalyst sensitivity to deactivation.
According to one embodiment, the low sulphur blended feed contains 5 to 95% wt. of a hydrocarbon cut originating from a gas-to-liquid process, preferably 20 to 80% wt. and more preferably 40 to 60% wt. According to one embodiment, the low-sulphur blended feed contains less than 70% aromatics, preferably less than 50% and more preferably less than 30%. According to one embodiment, the low-sulphur blended feed contains less than 15 ppm sulphur, preferably less than 8 ppm and more preferably less than 5 ppm.

According to one embodiment, the very low sulphur and very low aromatic hydrocarbon fluids have a boiling point in the range 150 to 400°C, preferably from 200 to 400°C. According to one embodiment, the very low sulphur and very low aromatic hydrocarbon fluids have a boiling range below 80°C, and preferably between 40 and 50°C. According to one embodiment, the very low sulphur and very low aromatic hydrocarbon fluids contain less than 300 ppm aromatics, preferably less than 100 ppm, and more preferably less than 50 ppm. According to one embodiment, the very low sulphur and very low aromatic hydrocarbon fluids have a sulphur content of less than 5 ppm, preferably less than 3 ppm, most preferably less than 0.5 ppm.

According to one embodiment, the process comprises three hydrogenation stages, preferably in three separate reactors. According to one embodiment, the process comprises a step of prefractionation of the low-sulphur blended feed prior to hydrogenation, into fractions having a boiling point in the range of 150 to 250°C or in the range of 220 to 330°C. According to one embodiment, the process further comprises a step of fractionation of the very low sulphur and very low aromatic hydrocarbon fluids into fluids of defined boiling ranges.

According to one embodiment, the very low sulphur and very low aromatic hydrocarbon fluids produced have:

- a naphthenic content below 60% wt., especially below 50% and even below 40%, and/or
- a polynaphthenic content below 30% wt., especially below 25% and even below 20%, and/or
- a paraffinic content above 40% wt., especially above 60% and even above 70%, and/or
- an isoparaffinic content above 20% wt., especially above 30%, and even above 40%.

These contents are those of the very low sulphur and very low aromatic hydrocarbon fluids after hydrogenation and before fractionation into fluids of defined boiling ranges. The invention also provides new hydrocarbon fluids obtainable by the process of the invention. Another object of the invention is the use of the hydrocarbon fluids as drilling fluids, as industrial solvents, in coating fluids, in metal extraction, in mining, in explosives, in concrete demoulding formulations, in adhesives, in printing inks, in metal working fluids, as cutting fluids, as rolling oils, as electric discharge machining (EDM) fluids, rust preventive in industrial lubricants, as extender oils, in sealants or polymers formulation with silicone, as viscosity depressants in plasticized polyvinyl chloride formulations, in resins, as crop protection fluids, in pharmaceutical products, in paint compositions, in polymers used in water treatment, paper manufacturing or printing pastes and cleaning solvents.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 represents the variation of the monoaromatics content in weight ppm as a function of the time for two feeds. One feed is a commercial ultra-low sulphur diesel. The other is a blend of 50/50 by weight of a gas-to-liquid gasoil (GTL) and the commercial ultra-low sulphur diesel used in the first feed.

DETAILED DESCRIPTION

To produce the specific fluids by the hydrogenation process according to the invention, the feedstock comprises a mixture of:

i) a hydrocarbon cut originating from a gas-to-liquid process in blend with
ii) at least one selected from the group consisting of: a hydrodeoxygenated hydrocarbon cut obtained from the biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof.

In one embodiment, the feedstock consists only of a mixture of:

i) a hydrocarbon cut originating from a gas-to-liquid process in blend with
ii) at least one selected from the group consisting of: a hydrodeoxygenated hydrocarbon cut obtained from the biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof.

Hydrocarbon Cut Originating from a Gas-To-Liquid Process

A Gas to liquids (GTL) process is a refinery process that converts natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons such as gasoline or diesel fuel. Methane-rich gases are converted into liquid synthetic fuels either via direct conversion or via syngas as an intermediate, for example using the Fischer-Tropsch process, Methanol to Gasoline process (MTG) or Syngas to gasoline plus process (STG+). For the Fischer Tropsch process, the effluents produced are Fischer-Tropsch derived.

By “Fischer-Tropsch derived” is meant that a hydrocarbon composition is, or derives from, a synthesis product of a Fischer-Tropsch condensation process. The Fischer-Tropsch reaction converts carbon monoxide and hydrogen into longer chain, usually paraffinic hydrocarbons:

\[ \text{n(CO) + nH}_2\text{O} \rightarrow \text{nCH}_x\text{H}_y + \text{nO}_2 + \text{heat} \]

in the presence of an appropriate catalyst and typically at elevated temperatures (e.g., 125 to 300°C, preferably 175 to 250°C) and/or pressures (e.g., 5 to 100 bars, preferably 12 to 50 bars). Hydrogen:carbon monoxide ratios other than 2:1 may be employed if desired. The carbon monoxide and hydrogen may themselves be derived from organic or inorganic, natural or synthetic sources, typically either from natural gas or from organically derived methane. For examples it can also be derived from biomass or from coal.

The collected hydrocarbon composition containing a continuous iso-paraffinic series as described above may preferably be obtained by hydroisomerisation of a paraffinic wax, preferably followed by dewaxing, such as solvent or catalytic dewaxing. The paraffinic wax is preferably a Fischer-Tropsch derived wax. Hydrocarbon cuts may be obtained directly from the Fischer-Tropsch reaction, or indirectly for instance by fractionation of Fischer-Tropsch synthesis products or preferably from hydrotreated Fischer-Tropsch synthesis products.
Hydrotreatment preferably involves hydrocracking to adjust the boiling range (see, e.g., GB-B-2077289 and EP-A-0147837) and/or hydroisomerisation, which can improve cold flow properties by increasing the proportion of branched paraffins. EP-A-0583836 describes a two-step hydrotreatment process in which a Fischer-Tropsch synthesis product is firstly subjected to hydroconversion under conditions such that it undergoes substantially no isomerisation or hydrocracking (this hydrogenates the olefinic and oxygen-containing components), and then at least part of the resultant product is hydroconverted under conditions such that hydrocracking and isomerisation occur to yield a substantially paraffinic hydrocarbon fuel. The desired gas oil fraction(s) may subsequently be isolated for instance by distillation.

Other post-synthesis treatments, such as polymerisation, alkylation, distillation, cracking-decarboxylation, isomerisation and hydrotreatment, may be employed to modify the properties of Fischer-Tropsch condensation products, as described for instance in U.S. Pat. No. 4,125,566 and U.S. Pat. No. 4,478,595. Examples of Fischer-Tropsch processes which for example can be used to prepare the above-described Fischer-Tropsch derived collected hydrocarbon composition are the so-called commercial Slurry Phase Distillate technology of Sasol, the Shell Middle Distillate Synthesis Process and the “AGC-21” Exxon Mobil process. These and other processes are for example described in more detail in EP-A-776959, EP-A-668342, U.S. Pat. No. 4,943,672, U.S. Pat. No. 5,059,299, WO-A-9934917 and WO-A-9920720. Typically, the gas to liquid feedstock shall contain less than 1 ppm sulphur as measured according to ASTM method D5453, less than 1 wt. % aromatics as measured according to method IP391, and have a density lower or equal to 0.800 g/cm³ as measured according to method ASTM D4052.

ii) Hydrocarbon Cuts of Fossil Origin, Gas Condensates, Hydrodeoxygenated Hydrocarbon Cuts from the Biomass:

a) According to the invention, solvent from biological origin used as feedstock in mixture can be produced from biological raw materials from the group consisting of vegetable oils, animal fats, fish oils, and mixtures thereof. Suitable biological raw materials include rapeseed oil, canola oil, colza oil, tall oil, sunflower oil, soybean oil, hemp oil, olive oil, linseed oil, mustard oil, palm oil, anchovy oil, castor oil, coconut oil, animal fats such as suet, tallow, lard, recycled animal fats, starting materials produced by genetic engineering, and botanical starting materials produced by microbes such as algae and bacteria. Condensation products, esters, or other derivatives obtained from biological raw materials may also be used as starting materials.

The solvent from biological origin is then produced by using for instance a process first comprising a hydrodeoxygenation (HDO) step for decomposing the structure of the biological ester or triglyceride constituent, and for removing oxygen, phosphorus and sulfur compounds, concurrently hydrogenating the olefinic bonds, followed by isomerization of the product thus obtained, thus branching the hydrocarbon chain and improving the low temperature properties of the paraffin. The product may for instance fractionate to give the desired fractions.

According to the invention typical refinery feeds can be of any type including feedstock from distillate hydrocracker unit, but also feedstock having high aromatic contents, such as standard ultra-low sulphur Diesel feedstock, heavy Diesel or jet type. The standard ultra-low sulphur Diesel contains less than 10 ppm sulphur as measured according to EN ISO 20846, has a density comprised between 0.820 and 0.845 g/cm³ as measured according to method EN ISO 12185, and generally meets the requirements of Euro V Diesel as defined in European Directive 2000/30/EC. It is generally obtained by a severe hydrodesulphurization of straight run gasoil cuts from atmospheric distillation.

Typical refinery feeds can also be hydrocracked to obtain shorter and simple molecules by the addition of hydrogen under high pressure in the presence of a catalyst. Descriptions of hydrocracking processes may be found in Hydrocarbon Processing of November 1996 pages 124 to 128, hydrocracking science and technology, 1996, U.S. Pat. No. 4,347,124, U.S. Pat. No. 4,447,315, WO-A-99/47626. The optionally hydrocracked feed is then blended with the hydrocarbon cut originating from a gas-to-liquid process and/or gas condensates and/or hydrodeoxygenated hydrocarbon cuts from the biomass in a proportion of 5 to 95 wt. % of GTL hydrocarbon cuts with respect to the weight of the feed, preferably 20 to 80 wt. % and more preferably 40 to 60 wt. %. Actually, the proportion of GTL hydrocarbon cut can be adapted so as to target a final density of about 0.800 to 0.820 g/cm³ which is commercially favourable.

c) gas condensates:

Gas Condensates derive from natural gas. They are a mixture of liquid hydrocarbons with more than four carbon atoms per molecule. Under natural conditions, a gas condensate is a solution of heavier hydrocarbons. The gas condensate separated from natural gas at reduced pressure and/or temperature by reverse condensation is a colorless or slightly colored liquid of density 700-800 kg/m³, which begins to boil at 30-70° C. The composition of a gas condensate corresponds approximately to the gasoline and kerosene fraction of crude oil or to a mixture of them. Ideally, according to the invention, blends of such feedstock, here the blended feeds, shall contain less than 15 ppm of sulphur, preferably less than 8 ppm and even more preferably less than 5 ppm as measured according to EN ISO 20846, less than 70% wt. aromatics, preferably less than 50% wt. and more preferably less than 30% wt. measured according to method IP391 or EN12916, and have a density inferior to 0.830 g/cm³ as measured according to method EN ISO 12185.

Before entering the hydrogenation unit, a pre-fractionation step can take place in the case where a gasoil cut feed is used. Having a more narrow boiling range entering the unit allows having a more narrow boiling range at the outlet. Indeed typical boiling ranges of pre-fractionated cuts are 150° C. to 250° C. or 220 to 330° C. while cuts without a pre-fractionating step typically have a boiling range from 150° C. to 360° C.

The optionally pre-fractionated low sulfur blended feeds are then hydrogenated. Hydrogen that is used in the hydrogenation unit is typically a high purity hydrogen, e.g. with a purity of more than 99%, albeit other grades can be used. Hydrogenation takes place in one or more reactors. The reactor can comprise one or more catalytic beds. Catalytic beds are usually fixed beds.

Hydrogenation takes place using a catalyst. Typical hydrogenation catalysts include but are not limited to: nickel, platinum, palladium, rhodium, nickel tung-

Oct. 6, 2016
In case the process makes use of 2 or 3 reactors, the first reactor will act as a sulphur trap, especially for benzo and di benzothiophens and their derivatives considered as the most refractory sulphur compounds present in refined gasoil cuts. This first reactor will thus trap substantially all the sulphur. The catalyst will thus be saturated very quickly and may be renewed from time to time. When regeneration or rejuvenation is not possible for such saturated catalyst the first reactor is considered as a sacrificial reactor which size and catalyst content both depend on the catalyst renewal frequency.

In an embodiment the resulting product and/or separated gas is/are at least partly recycled to the inlet of the hydrogenation stages. This dilution helps maintaining the exothermicity of the reaction within controlled limits, especially at the first stage. Recycling also allows heat-exchange before the reaction and also a better control of the temperature. The stream exiting the hydrogenation unit contains the hydrogenated product and hydrogen. Flash separators are used to separate effluents into gas, mainly remaining hydrogen, and liquids, mainly hydrogenated hydrocarbons. The process can be carried out using three flash separators, one of high pressure, one of medium pressure, and one of low pressure, very close to atmospheric pressure.

The hydrogen gas that is collected on top of the flash separators can be recycled to the inlet of the hydrogenation unit or at different levels in the hydrogenation units between the reactors. Because the final separated product is at about atmospheric pressure, it is possible to feed directly the fractionation stage, which is preferably carried out under vacuum pressure that is at about between 10 to 50 mbar, preferably about 30 mbar. The fractionation stage can be operated such that various hydrocarbon fluids can be withdrawn simultaneously from the fractionation column, and the boiling range of which can be predetermined.

The hydrogenation reactions, the separators and the fractionation unit can thus be connected directly, without having to use intermediate tanks, as is usually the case in the prior art documents. By adopting the feed, especially the initial and final boiling points of the feed, it is possible to produce directly, without intermediate storage tanks, the final products with the desired initial and final boiling points. Moreover, this integration of hydrogenation and fractionation allows an optimized thermial integration with reduced number of equipment and energy savings. The temperature in the reactors is typically about 150-160° C. and the pressure is typically about 140 bars while the liquid hourly space velocity is typically about 0.8 and the treat rate is typically about 100 to 180 Nm³/ton of feed, depending on the feed quality.

The fluids produced according to the process of the invention possess outstanding properties, in terms of aniline point or solvency power, molecular weight, vapour pressure, viscosity, defined evaporation conditions for systems where drying is important, and defined surface tension. The fluids produced according to the process of the invention have a boiling range from 100 to 400° C. and also exhibit an enhanced safety, due to the very low aromatics content, typically less than 300 ppm, more preferably less than 100 ppm, and even more preferably less than 50 ppm. This makes them suitable for use in crop protection fluids as well as in pharmaceutical products. This is especially useful for high temperature boiling products, typically products boiling in the range 300-400° C., preferably 320-380° C.
The boiling range of the final product is preferably not more than 80°C, preferably not more than 65°C, more preferably not more than 50°C. The fluids prepared according to the process of the present invention also have an extremely low sulphur content, typically less than 5 ppm, even less than 3 ppm and preferably less than 0.5 ppm, at a level too low to be detected by the usual low-sulphur analyzers.

The fluids produced by the process of the present invention have a variety of uses for example in drilling fluids, in hydraulic fracturing, in mining, in water treatments, in industrial solvents, in paints composition, in explosives, in printing inks, in oil dispersants, in food processing industry and in metal working fluids, such as cutting fluids, electric discharge machining (EDM) fluids, rust preventives, coating fluids and aluminium rolling oils, and in concrete demoulding formulations. They can also be used in industrial lubricants such as shock absorbers, insulation oils, hydraulic oils, gear oils, turbine oils, textile oils and in transmission fluids such as automatic transmission fluids or manual gear box formulations.

In all this foreshem uses, the Initial Boiling Point (IBP) to Final Boiling Point (FBP) range is selected according to the particular use and composition. The fluids are also useful as components in adhesives, sealants or polymer systems such as silicone sealant, modified silane polymers where they act as extender oils and as viscosity depressants for polyvinyl chloride (PVC) pastes or Plastisol formulations.

The fluids produced according to the process of the present invention may also be used as new and improved solvents, particularly as solvents for resins. The solvent-resin composition may comprise a resin component dissolved in the fluid, the fluid comprising 5 to 95% by total volume of the composition. The fluids produced according to the process of the present invention may be used in place of solvents currently used for inks, coatings and the like. The fluids produced according to the process of the present invention may also be used to dissolve resins such as: acrylic-thermoplastic, acrylic-thermosetting, chlorinated rubber, epoxy (either one or two part), hydrocarbon (e.g., olefins, terpene resins, rosin esters, petroleum resins, coumarone-indene, styrene-butadiene, styrene, methyl-styrene, vinyl-vinylidene-hydrogenated polyvinyl chloride and isobutylene), phenolic, polyester and alkyd, polyurethane and modified polyurethane, silicone and modified silicone (MS polymers), urea, and, vinyl polymers and polyvinyl acetate.

Examples of the type of specific applications for which the fluids and fluid-resin blends may be used include coatings, cleaning compositions and inks. For coatings the blend preferably has high resin content, i.e., a resin content of 20% to 80% by volume. For inks, the blend preferably contains a lower concentration of the resin, i.e., 5%-30% by volume. In yet another embodiment, various pigments or additives may be added.

The fluids produced by the process of the present invention can be used as cleaning compositions for the removal of hydrocarbons. The fluids may also be used in cleaning compositions such as for use in removing ink, more specifically in removing ink from printing.

In the offset printing industry it is important that ink can be removed quickly and thoroughly from the printing surface without harming the metal or rubber components of the printing machine. Further there is a tendency to require that the cleaning compositions are environmentally friendly in that they contain no or hardly any aromatic volatile organic compounds and/or halogen containing compounds. A further trend is that the compositions fulfill strict safety regulations. In order to fulfill the safety regulations, it is preferred that the compositions have a flash point of more than 62°C, more preferably a flash point of 90°C or more. This makes them very safe for transportation, storage and use. The fluids produced according to the process of the present invention have been found to give a good performance in that ink is readily removed while these requirements are met.

The fluids produced according to the process of the invention are also useful as drilling fluids, such as a drilling fluid which has the fluid prepared by the process of this invention as a continuous oil phase. The fluid may also be used as a penetration rate enhancer comprising a continuous aqueous phase containing the fluid produced according to the process of the invention dispersed therein.

Fluids used for offshore or on-shore applications need to exhibit acceptable biodegradability, human, ecotoxicity, eco-accumulation and lack of visual sheen credentials for them to be considered as candidate fluids for the manufacturer of drilling fluids. In addition, fluids used in drilling uses need to possess acceptable physical attributes. These generally include a viscosity less than 4.0 mm²/s at 40°C, a flash value of less than 100°C and, for cold weather applications, a pour point at -40°C or lower. These properties have typically been only attainable through the use of expensive synthetic fluids such as hydrogenated polyalkaolefins, as well as unsaturated internal olefins and linear alpha-olefins and esters. The properties can however be obtained in some fluids produced according to the process of the present invention.

Drilling fluids may be classified as either water-based or oil-based, depending upon whether the continuous phase of the fluid is mainly oil or mainly water. Water-based fluids may however contain oil and oil-based fluids may contain water and the fluids produced according to the process of the invention are particularly useful as the oil phase.

Typically preferred ASTM D-86 boiling ranges for the uses of the fluids are that of printing ink solvents (sometimes known as distillates) have boiling ranges in the ranges of 235°C to 265°C, 260°C to 290°C, 280°C to 315°C and 300°C to 355°C. Fluids preferred for use as drilling fluids have boiling ranges in the ranges of 195°C to 240°C, 235°C to 265°C and 260°C to 290°C. Fluids preferred for explosives, concrete demoulding, industrial lubricants, transmission fluids and metal working fluids have boiling ranges in the ranges of 185°C to 215°C, 195°C to 240°C, 235°C to 365°C, 260°C to 290°C, 280°C to 325°C and 300°C to 360°C. Fluids preferred as extenders for sealants have boiling ranges in the ranges of 195°C to 240°C, 235°C to 265°C, 260°C to 290°C, 280°C to 325°C or 300°C to 360°C. Fluids preferred as viscosity depressants for polyvinyl chloride plastisols have boiling ranges in the ranges of 185°C to 215°C, 195°C to 240°C, 235°C to 265°C, 260°C to 290°C, 280°C to 315°C and 300°C to 360°C.

Fluids preferred as carrier for polymeric composition used in water treatment, mining operation or printing pastes have boiling ranges in the ranges of 185°C to 215°C.
C., 195° C. to 240° C., 235° C. to 260° C., 260° C. to 290° C., 280° C. to 315° C. and 300° C. to 360° C. Fluids preferred for crop protection application have boiling ranges in the range of 300 and 370° C., such fluids being used in combination with hydrocarbon fluids such as isodewaxed hydrocarbons or any hydrocarbons having comparable properties such as viscosity. For pharmaceutical application, suitable fluids are those having boiling ranges in the ranges of 275° C. to 330° C., 290° C. to 380° C. and 300° C. to 370° C. For paint compositions and cleaning applications, the most preferred boiling ranges are in the ranges of 140 to 210° C., and 180 to 220° C. Fluids showing an initial boiling point above 250° C. and a final boiling point close to 330° C. or preferably close to 290° C. will be preferred for low VOC coatings formulations.

**EXAMPLE**

[0072] The following example illustrates the invention without limiting it.

Example 1

[0073] The aim of the present example is to describe the preparation of hydrocarbon fluids according to the process of the present invention. In the present invention, a commercial ultra-low sulphur Diesel (commercial ULSD having a sulphur content of 8 ppm, a density of 0.845 g/cm³, an aromatics content of 28 wt. % and a mono aromatics content of 22.7 wt. %) is blended with a gasoil cut originating from a gas-to-liquid process (GTL gasoil), having a sulphur content inferior to 1 ppm, a density of 0.768 g/cm³, an aromatics content inferior to 1 wt. % and a mono aromatics content of 563 ppm in a 50/50 proportion in order to obtain blend A having the following characteristics: 4 ppm sulphur, 14 wt. % aromatics, 11.4 wt. % of mono aromatics, and a density of 8.06 g/cm³.

[0074] Blend A is then further hydrogenated to be deoxygenated in presence of a nickel hydrogenating catalyst according to the process of the invention under a pressure of 130 bars, at a liquid hourly space velocity (LHSV) of 1 h⁻¹ and at temperature between 155 and 160° C. Then the resulting hydrogenated desulphurized distillate is fractionated into different cuts, the main one showing the characteristics given in table 1 hereafter.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>units</th>
<th>Methods</th>
<th>Example 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15° C.</td>
<td>kg/m³</td>
<td>ASTM D4052</td>
<td>808</td>
</tr>
<tr>
<td>Saybolt colour</td>
<td>° C.</td>
<td>ASTM D56</td>
<td>&gt;+30</td>
</tr>
<tr>
<td>Flash point</td>
<td>° C.</td>
<td>ASTM D93</td>
<td>115</td>
</tr>
<tr>
<td>Sulphur content</td>
<td>ppm</td>
<td>ASTM D543</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Distillation IBP</td>
<td>° C.</td>
<td>ASTM D86</td>
<td>252</td>
</tr>
<tr>
<td>Distillation FBP</td>
<td>° C.</td>
<td>ASTM D86</td>
<td>328</td>
</tr>
<tr>
<td>Aromatics content</td>
<td>ppm</td>
<td>UV method</td>
<td>85</td>
</tr>
</tbody>
</table>

These results show that the product prepared according to the process of the invention is free of sulphur and exhibits a very low aromatic content. Its properties make it very suitable for hydrocarbon fluid applications.

[0075] FIG. 1 shows the variation of the mono aromatic content in the effluent after the hydrogenation step for both blend A and the commercial ultra-low sulphur diesel alone according to the example. When the commercial ultra-low sulphur diesel alone is hydrogenated, the content of mono aromatic of the effluent at the start of hydrogenation is very high (about 100 ppm) and increases progressively up to about 160 ppm 50 hours after the start of the hydrogenation. In comparison, when the blend A is hydrogenated, the mono aromatics content in the effluent at the start of hydrogenation is only about 25 ppm. It remains stable and very low in the time. Indeed, it reaches only about 40 ppm 50 hours after the start of the hydrogenation.

[0076] These results indicate that:

1) at the start of the hydrogenation, the mono aromatics content for feed A is 4 times lower than that of the commercial ultra-low sulphur diesel alone (25 ppm for feed A versus 100 ppm for the commercial ultra-low sulphur diesel alone). This result is surprising since before hydrogenation, the mono aromatics content for feed A was only 2 times lower than that of the commercial ultra-low sulphur diesel alone. Indeed, the content of mono aromatics in the commercial ultra-low sulphur Diesel before hydrogenation was 28 wt. % and the content of mono aromatic contents in blend A before hydrogenation was 14 wt. %. The hydrogenation process is thus more efficient when applied to blend A than when applied to the commercial ultra-low sulphur diesel alone.

2) with the commercial ultra-low sulphur diesel alone, in addition to the impossibility to obtain the desired characteristics of the hydrogenated desulphurized distillate with respect to the mono aromatics content, a strong catalyst deactivation is observed. The strong catalyst deactivation is indicated by the fact that the mono aromatic content reaches 150 ppm 50 hours after the start of hydrogenation. In contrast for blend A, the mono aromatic content remains stable at about 40 ppm 20-50 hours after the start of hydrogenation. These results show the advantage of adding a hydrocarbon cut originating from a gas-to-liquid process to a feed selected from the group consisting of a hydrodeoxygenated hydrocarbon cut obtained from biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof.

1. A process for hydrogenating a low sulphur blended feed containing less than 15 ppm of sulphur into very low sulphur and very low aromatic hydrocarbon fluids containing less than 5 ppm of sulphur and less than 300 ppm of aromatics and having a boiling point in a range of from 100 to 400° C. and a boiling range of not more than 80° C., the low-sulphur blended feed comprising a mixture of:
   i) a hydrocarbon cut originating from a gas-to-liquid process with
   ii) at least one selected from a group comprising a hydrodeoxygenated hydrocarbon cut obtained from biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof;
   the process further comprising catalytically hydrogenating the feed at a temperature from 80 to 180° C. and at a pressure from 50 to 160 bars.

2. The process of claim 1, wherein the low sulphur blended feed contains 5 to 95% wt. of a hydrocarbon cut originating from a gas-to-liquid process.

3. The process of claim 1, wherein the low-sulphur blended feed contains less than 70% aromatics.

4. The process of claim 1, wherein the low-sulphur blended feed contains less than 8 ppm sulphur.

5. The process of claim 1, wherein the very low sulphur and very low aromatic hydrocarbon fluids have a boiling point in the range 150 to 400° C.
6. The process of claim 1, wherein the very low sulphur and very low aromatic hydrocarbon fluids have a boiling range below 80°C.
7. The process of claim 1, wherein the very low sulphur and very low aromatic hydrocarbon fluids contain less than 100 ppm aromatics.
8. The process of claim 1, wherein the very low sulphur and very low aromatic hydrocarbon fluids have a sulphur content of less than 3 ppm.
9. The process of claim 1, comprising three hydrogenation stages in three separate reactors.
10. The process of claim 1, further comprising prefractionation of the low-sulphur blended feed prior to hydrogenation, into fractions having a boiling point in the range of 150 to 250°C or in the range of 220 to 330°C.
11. The process of claim 1, further comprising fractionation of the very low sulphur and very low aromatic hydrocarbon fluids into fluids of defined boiling ranges.
12. The process of claim 1, wherein the very low sulphur and very low aromatic hydrocarbon fluids thus produced have:
   a naphthenic content below 60% wt, and/or
   a polynaphthenic content below 30% wt, and/or
   a paraffinic content above 40% wt, and/or
   an isoparaffinic content above 20% wt.
13. Hydrocarbon fluids comprising a low sulphur blended feed containing less than 15 ppm of sulphur into very low sulphur and very low aromatic hydrocarbon fluids containing less than 5 ppm of sulphur and less than 300 ppm of aromatics and having a boiling point in a range of from 100 to 400°C and a boiling range of not more than 80°C, the low-sulphur blended feed comprising a mixture of:
   i) a hydrocarbon cut originating from a gas-to-liquid process
   ii) at least one selected from a group comprising a hydrodeoxygenated hydrocarbon cut obtained from biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof.
14. A process for hydrogenating a low sulphur blended feed containing less than 15 ppm of sulphur into very low sulphur and very low aromatic hydrocarbon fluids containing less than 5 ppm of sulphur and less than 300 ppm of aromatics and having a boiling point in a range of from 100 to 400°C and a boiling range of not more than 80°C, the low-sulphur blended feed comprising a mixture of:
   i) a hydrocarbon cut originating from a gas-to-liquid process with
   ii) at least one selected from a group comprising a hydrodeoxygenated hydrocarbon cut obtained from biomass, a gas condensate, a hydrocarbon cut of fossil origin and mixtures thereof;
the process further comprising catalytically hydrogenating the feed at a temperature from 80 to 180°C and at a pressure from 50 to 160 bars;
the hydrocarbon fluids being at least one of: drilling fluids, industrial solvents, coating fluids, metal extraction fluids, mining fluids, explosives, concrete demoulding formulations, adhesives, printing inks, metal working fluids, cutting fluids, rolling oils, electric discharge machining (EDM) fluids, rust preventive in industrial lubricants, extender oils, sealants or polymers formulation with silicone, viscosity depressants in plasticised polyvinyl chloride formulations, resins, crop protection fluids, pharmaceutical products, paint compositions, polymers used in water treatment, paper manufacturing or printing pastes or cleaning solvents.
* * * * *