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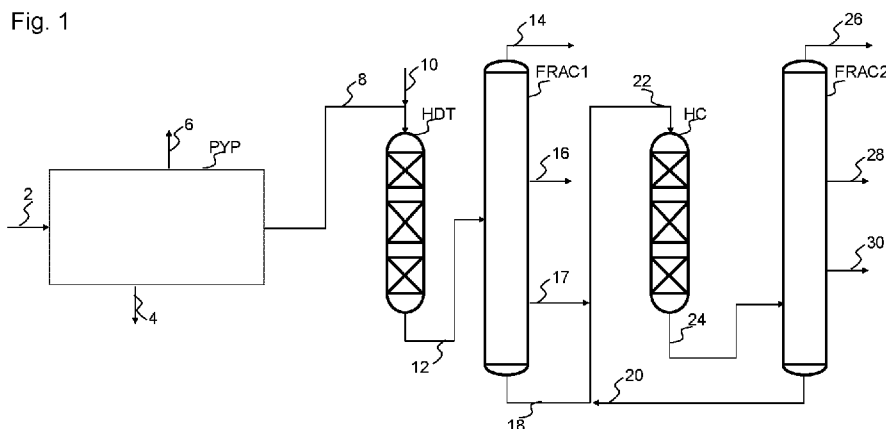
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## (54) Title: PROCESS FOR PRODUCTION OF TRANSPORTATION FUEL

Fig. 1



(57) Abstract: The present disclosure relates to a process and a process plant for production of a hydrocarbon composition useful as a transportation fuel according to a commercial transportation fuel specification from a hydrocarbonaceous feedstock comprising at least 0.5 wt% oxygen and at least 25 wt% carbon in cyclic structures, comprising the steps of a. directing a hydrocarbonaceous feedstock to hydrotreatment in one or more steps providing an intermediate product comprising less than 0.1 wt% oxygen and a specific gravity, for the fraction boiling in the range defined by the commercial transportation fuel specification, above the upper limit of specific gravity under the commercial transportation fuel specification, b. providing a hydrotreated hydrocarbon stream for hydroconversion from said intermediate product optionally by fractionation, wherein said fraction for hydroconversion has a T50 being below T95 of the commercial transportation fuel specification, c. directing the stream for hydroconversion to contact a hydroconversion catalyst under hydroconversion conditions to provide a hydroconverted hydrocarbon stream, d. fractionating said hydroconverted hydrocarbon stream to provide at least said hydrocarbon composition useful as a transportation fuel.

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## Description

### Title of Invention : Process for production of transportation fuel

#### Technical Field

[0001] The present invention relates to a process for production of quality transportation fuels by hydroconversion of liquid cyclic hydrocarbonaceous feedstocks which may be formed from solid hydrocarbonaceous materials e.g. tires or lignocellulosic solids by thermochemical decomposition.

#### Background Art

[0002] Thermochemical decomposition such as pyrolysis or hydrothermal liquefaction (HTL) of certain raw materials having an aromatic structure, such as waste tires and rubber, will provide liquids (for convenience pyrolysis oil) having a high content of ring structures like aromatics and naphthenes. Similar liquids may also be provided as tar from coke ovens and pyrolysis of lignite. While a large fraction of such pyrolysis oil boils in the middle distillate range, the dominance of cyclic compounds means that such cyclic pyrolysis oil boiling in the middle distillate range is not suited for use as a quality middle distillate transportation fuel.

#### Summary of Invention

[0003] We have now identified a process with a potential for conversion of such cyclic pyrolysis oil to middle distillate transportation fuel, involving treatment of the cyclic pyrolysis oil boiling in the middle distillate range in the presence of a hydroconversion catalyst at elevated pressure.

[0004] When a feedstock, such as pyrolysis oil, boils above the boiling point range of the desired products it is known to practice hydrocracking on this feedstock to reduce the molecular weight, and thus the boiling point, of the feedstock. Since hydrocracking is associated with a loss of product yield, it is common practice to fractionate the feedstock by distillation, such that only feedstock boiling above the desired range is directed to hydrocracking, in order to minimize loss of product yield.

[0005] However, according to the present disclosure, we have identified that when directing a cyclic feedstock having a boiling point range overlapping the desired boiling point range to hydroconversion, a high yield of quality transportation fuel may be obtained.

[0006] The process will be more selective towards saturation of aromatics as well as addition of hydrogen to cyclic structures if the hydrogen partial pressure is elevated, e.g. by increasing the total process pressure.

## Definitions

[0007] As used herein, the term “thermochemical decomposition” shall for convenience be used broadly for any decomposition process, in which a material is partially decomposed at elevated temperature (typically 250°C to 800°C or even 1000°C), in the presence of substoichiometric amount of oxygen (including no oxygen). The product will typically be a combined liquid and gaseous stream, as well as an amount of solid char. The term shall be construed to include processes known as pyrolysis and hydrothermal liquefaction, both in the presence and absence of a catalyst.

[0008] For simplicity all products from thermochemical decomposition, such as pyrolysis and thermal liquefaction, will in the following be referred to as pyrolysis oil, irrespective of the nature of the originating process.

[0009] Where concentrations in the gas phase are given, they are, unless otherwise specified given as molar concentration.

[0010] In the following the abbreviation vol% shall be used to signify volume percentage for a gas.

[0011] Where concentrations in liquid or solid phase are given, they are, unless otherwise specified given as weight concentrations.

[0012] In the following the abbreviation ppm<sub>w</sub> shall be used to signify weight parts per million, e.g. the mass of sulfur atoms relative to the mass of a liquid hydrocarbon stream.

[0013] In the following the abbreviation wt% shall be used to signify weight percentage.

[0014] The term aromatic molecule shall for the purpose of the present application be used to signify homocyclics with a conjugated stable bond structure in accordance with IUPAC terminology, comprising only carbon atoms in the aromatic ring, as well as heterocyclics, comprising one or more atoms other than carbon and hydrogen, such as oxygen, sulfur and nitrogen. The term shall also cover both conjugated monocyclics and polycyclics, including fused aromatics.

[0015] The aromatic content of a liquid is in accordance with the art the total mass of molecules having at least one aromatic structure, relative to the total mass of all molecules in %.

[0016] The content of carbon in cyclic structures is in accordance with the definition of aromatic content the total mass of carbon atoms in molecules having at least one cyclic structure, relative to the total mass of carbon in all molecules in %.

[0017] The pressure and temperature shall in accordance with the terminology of the skilled person of refinery technology in the following be construed as the pressure and temperature respectively at the inlet of a reactor.

[0018] The hydrogen partial pressure shall be construed as the partial pressure of hydrogen in the treat gas.

[0019] The space velocity shall in accordance with the terminology of the skilled person of refinery technology in the following be construed as the LHSV (liquid hourly space velocity) over a single catalytically active material unless otherwise indicated.

[0020] The initial boiling point (IBP), the final boiling point (FBP) and the temperatures corresponding to recovered amounts of sample, shall be understood in accordance with the ASTM D86 standard. T5, T10, T50 and T95 boiling points shall accordingly be understood as the distillation temperatures where 5vol%, 10vol%, 50vol% and 95vol% respectively have been recovered.

## **Detailed description**

[0021] Conversion of biomass and waste to liquid products by thermochemical decomposition, such as pyrolysis and thermal liquefaction, is, especially with subsequent hydrotreatment, considered an environmentally friendly source for alternatives to petroleum products, especially from a global warming perspective.

Due to the nature of these liquid products (for simplicity pyrolysis oil, irrespective of the originating process) they will require upgrading, e.g. by hydrotreatment to remove heteroatoms, such as sulfur and oxygen, and to hydrogenate olefinic structures. The nature of formation means that the products are not stabilized, and therefore, contrary to typical fossil raw feedstocks, they may be very reactive, demanding high amounts of hydrogen, releasing significant amounts of heat during reaction and furthermore having a high propensity towards polymerization. The release of heat may increase the polymerization further, and at elevated temperature catalysts may also be deactivated by coking.

[0022] The thermochemical decomposition process plant section providing the hydrocarbonaceous feedstock according to the present disclosure may be in many forms including rotary oven, fluidized bed, transported bed, or circulating fluid bed, as is well known in the art. This decomposition converts a pyrolysis feedstock into a solid (char), a high boiling liquid (tar) and fraction being gaseous at elevated temperatures. The gaseous fraction comprises a fraction condensable at standard temperature (pyrolysis oil or condensate, C<sub>5</sub>+ compounds) and a non-condensable fraction (pyrolysis gas, including pyrolysis off-gas). For instance, the thermochemical decomposition process plant section (the pyrolysis section) may comprise a pyrolizer unit (pyrolysis reactor), cyclone(s) and/or filters to remove particulate solids such as char, and a cooling unit for thereby producing pyrolysis off-gas stream and said pyrolysis oil stream, i.e. condensed pyrolysis oil. The pyrolysis gas stream comprises light hydrocarbons e.g. C<sub>1</sub>-C<sub>4</sub> hydrocarbons, and commonly also H<sub>2</sub>O, CO and CO<sub>2</sub>. Typically, the term pyrolysis oil comprises condensate and tar, and the pyrolysis oil stream from pyrolysis of biomass may also be referred to as bio-oil or bio-crude. The pyrolysis oil is a liquid substance rich in blends of molecules, usually consisting of more than two hundred different compounds mainly oxygenates such as acids, sugars, alcohols, phenols, guaiacols, syringols, aldehydes, ketones, furans, and other mixed oxygenates, resulting from the depolymerization of the solids treated in pyrolysis. Thermochemical decomposition of non-biological waste comprising suitable compositions, such as plastic fractions or rubber, including end of life tires will only provide products which contain low concentrations of oxygen, unless oxygen is added to the decomposition process

and will commonly provide a hydrocarbonaceous feedstock which has a structure similar to that of tar from coke ovens.

[0023] For the purposes of the present invention, the pyrolysis section may be fast pyrolysis, also referred to in the art as flash pyrolysis. Fast pyrolysis means the thermochemical decomposition of a solid renewable feedstock typically in the absence of oxygen, at temperatures typically in the range 350-650°C e.g. about 500°C and reaction times of 10 seconds or less, such as 5 seconds or less, e.g. about 2 sec. Fast pyrolysis may for instance be conducted by autothermal operation e.g. in a fluidized bed reactor. The latter is also referred to as autothermal pyrolysis and is characterized by employing air, optionally with an inert gas or recycle gas, as the fluidizing gas. Thereby, the partial oxidation of pyrolysis compounds being produced in the pyrolysis reactor (autothermal reactor) provides the energy for pyrolysis while at the same time improving heat transfer. In so-called catalytic fast pyrolysis, a catalyst may be used. An acid catalyst, commonly comprising a zeolite, without active metals, may be used to upgrade the pyrolysis vapors, and it can both be operated in an in-situ mode (the catalyst is located in the pyrolysis reactor) and an ex-situ mode (the catalyst is placed in a separate reactor). The use of a catalyst conveys the advantage of helping to stabilize the pyrolysis oil and thereby making it easier to hydroprocess. In addition, increased selectivity towards desired pyrolysis oil compounds may be achieved.

[0024] In some cases, hydrogen is added to the catalytic pyrolysis which is then called reactive catalytic fast pyrolysis. If the catalytic pyrolysis is conducted at a high hydrogen pressure, such as above 0.5 MPa, it is often called catalytic hydrolysis. The catalyst for upgrading in the presence of hydrogen, will typically comprise one or more metals active in hydrogenation, such as a metal from Group 6 or Group 8,9 or 10.

[0025] The pyrolysis stage may be fast pyrolysis which is conducted without the presence of a catalyst and hydrogen, i.e. the fast pyrolysis stage is not catalytic fast pyrolysis, hydrolysis or catalytic hydrolysis. This enables a much simpler and inexpensive process.

[0026] The thermochemical decomposition section may also be hydrothermal liquefaction. Hydrothermal liquefaction means the thermochemical conversion of solid waste and biomass into liquid fuels by processing in a hot, pressurized water environment for sufficient time to break down the solid polymeric structure to mainly liquid components. Typical hydrothermal processing conditions are temperatures in the range of 250-375°C or even up to 500°C and operating pressures in the range of 4-40 MPa. This technology offers the advantage of operation of a lower temperature, higher energy efficiency and producing a product with a lower oxygen content compared to pyrolysis, e.g. fast pyrolysis.

[0027] Finally, other relevant thermochemical decomposition methods are intermediate or slow pyrolysis, in which the conditions involve a lower temperature and commonly higher residence times – these methods may also be known as carbonization or torrefaction. The major benefit of these thermochemical decomposition methods is a lower investment, but they may also have specific benefits for specific feedstocks or for specific product requirements, such a need for bio-char.

[0028] When high amounts of solid product are produced, such as processes producing bio-char or when retrieval of unconverted carbon black particles from thermochemical conversion of end-of-life tires is desired, it may be beneficial to filter the liquid product as part of the thermochemical conversion process, which will also have the benefit of minimizing deactivation of downstream catalyst.

[0029] The conversion of a hydrocarbonaceous feedstock comprising oxygenates to hydrocarbons is a common process for production of renewable transportation fuels from oils and fats, but the reactivity and other specifics differ for different feedstocks. The cyclic hydrocarbonaceous feedstock of the present disclosure typically comprises a high amount of cyclic structures and may also comprise oxygenates taken from the group consisting of ketones, aldehydes or alcohols, but commonly only low amounts of carboxylic acids. It may originate from thermochemical decomposition of non-biological waste such as plastic and rubber fractions, including end of life tires, as well as from biological materials rich in lignin, such as straw and waste from wood processing or solid fossil feedstocks such as lignite, typically after a thermal and/or catalytic degradation process. When the feedstock is of biological origin, the feedstock and the product



will be characterized by having a  $^{14}\text{C}$  content above 0.5 parts per trillion of the total carbon content, but when the feedstock includes waste of fossil origin, such as plastic, this ratio may be different.

[0030] The production of hydrocarbon products typically requires one or more hydroprocessing steps which most commonly are; hydrotreatment for removing heteroatoms and saturating double bonds, hydroisomerization for adjusting hydrocarbon molecule structure and hydroconversion for reducing hydrocarbon molecular weight, and according to the present disclosure, hydrodearomatization is also of relevance. During hydrotreatment, the hydrocarbonaceous feedstock is combined with an excess of hydrogen and react in hydrodeoxygenation processes, where water is released from the oxygenates. If the oxygenates involve carbonyl groups, decarboxylation and decarbonylation processes releasing carbon dioxide and carbon monoxide may also take place, and in that case an equilibrium between carbon dioxide and carbon monoxide exists according to the water/gas shift process, but this is less common in the types of cyclic hydrocarbonaceous feedstock according to the present disclosure. For pyrolysis oil originating from rubber and plastic, the oxygen content will be low, such as from 0.5 wt% and up to 5wt%, whereas for pyrolysis oil from ligneous compounds it will be higher, such as, from 5 wt%, 10 wt% or even 25 wt% to 50wt% of the oxygenate feedstock is oxygen, and thus a significant amount of the product stream will be water, carbon dioxide and carbon monoxide. In addition, an amount of light hydrocarbons may also be present in the product stream, depending on the nature of the feedstock and the side reactions occurring. Hydrotreatment may also involve extraction of other hetero-atoms, notably nitrogen and sulfur but possibly also halogens and silicon as well as the saturation of double bonds. Especially the hydrotreatment of oxygenates is very reactive and exothermal, and moderate or low activity catalysts may be preferred to avoid excessive heat release and runaway reactions resulting in coke formation deactivating the catalyst. The catalyst activity is commonly controlled by only using low amounts of active metals and especially limiting the amount of promoting metals, such as nickel and cobalt. Commonly such a material with moderate activity is followed by a more active material, ensuring close to complete hydrotreatment.

The material catalytically active in hydrotreatment may commonly comprise from at least 1 wt%, at least 5 wt% or at least 8 wt% to at most 15 wt%, at most 20 wt% or at most 25 wt% molybdenum or tungsten, promoted by an amount of nickel in the range from 0.01:1 Ni:Mo+W to 0.1:1 Ni:Mo+W (where the ratios designate molar ratios between the amount of Ni and the total amount of Mo and W) on a refractory oxidic support such as alumina, silica or titania, which typically is amorphous. A corresponding active catalyst may comprise a higher amount of Ni, such as 0.1:1 Ni:Mo+W to 0.5:1 Ni:Mo+W, whereas even more elevated ratios would typically correspond to hydrodearomatization catalysts. In these compositions cobalt may have an effect similar to that of nickel. The catalyst may comprise further components, such as boron or phosphorous in combination with the active metals and/or the support. The conditions are typically a temperature in the interval 250-400°C, a pressure in the interval 3-15 MPa, and a liquid hourly space velocity (LHSV) in the interval 0.1-2 hr<sup>-1</sup>. The deoxygenation will involve a combination of hydrodeoxygenation producing water and if the oxygenates comprise carboxylic groups such as acids or esters, decarboxylation producing CO<sub>2</sub>. The deoxygenation of carboxylic groups, if present, may proceed by hydrodeoxygenation or decarboxylation with a selectivity which, depending on conditions and the nature of the catalyst may vary from above 90% hydrodeoxygenation to above 90% decarboxylation. Similarly, sulfur is removed by hydrodesulfurization, typically producing H<sub>2</sub>S. Hydrodesulfurization and deoxygenation by both routes is exothermal, and with the presence of a high amount of oxygen, the process may involve intermediate cooling e.g. by quenching with cold hydrogen, feed or product. The feedstock may preferably contain an amount of sulfur to maintain sulfidation of the metals, in order to maintain their activity. If the feedstock stream comprising oxygenates comprises less than 10, 100 or 500 ppm<sub>w</sub> sulfur, a sulfide donor, such as dimethyldisulfide (DMDS) has typically been added to the feed.

[0031] If the unstabilized feedstock is highly reactive, a pre-treatment at moderate conditions may be relevant, to stabilize the feedstock. This may involve an inlet temperature as low as 80°C, 120°C or 200°C, a pressure in the interval 3-15 MPa, and a liquid hourly space velocity (LHSV) in the interval 0.1-2 hr<sup>-1</sup> and a deliberate choice of less active catalyst, such as unpromoted or weakly promoted

molybdenum e.g. in a concentration from 5 wt% to 15 wt% on a refractory support. Due to the reactive components and the exothermal nature thermal control by quenching or recycle may be relevant in this pre-treatment step.

[0032] When the structure of the feedstock is cyclic, the hydrotreatment process may provide a product rich in aromatic molecules and naphthenes. These molecules have poor diesel properties, including density (specific gravity) and cetane index. Traditionally aromatic molecules have been converted by saturation over a hydrotreatment catalyst. As the equilibrium between aromatic and non-aromatic rings favors aromatics at high temperature, moderate temperatures and thus high activity catalysts have been preferred, which has implied use of noble metals, which are catalytically active at lower temperatures than sulfided base metals. However, for typical hydrocarbonaceous feedstocks from thermochemical decomposition of cyclic solid materials, merely saturating the aromatic structures may not be sufficient to obtain a density or a cetane index value in compliance with diesel fuel specifications, and therefore additional measures are required.

[0033] Hydroconversion chemically involves the breaking of carbon-carbon bonds in hydrocarbons by addition of hydrogen. This process is typically used in the form of hydrocracking to adjust the boiling point characteristics of a hydrocarbon mixture, by cracking large molecules into smaller, but the breaking of carbon-carbon bonds will also have the effect of opening rings in cyclic molecules. This ring-opening will have the related effect of shifting the equilibrium of hydrodearomatization by converting the non-aromatic product such that this reaction no longer is equilibrium limited, and thus ring-opening will indirectly have the effect of reducing the content of aromatics. Typically, hydroconversion involves directing an intermediate feedstock to contact a hydroconversion catalyst comprising an active metal (either elemental noble metals such as platinum and/or palladium or sulfided base metals such as nickel, cobalt, tungsten and/or molybdenum), an acidic support (typically a molecular sieve showing high activity in breaking carbon-carbon bonds, and having a topology such as MFI, BEA and FAU) and a refractory support (such as alumina, silica or titania, or combinations thereof). The catalyst may comprise further components, such as boron or phosphorous. The conditions are typically a temperature in the interval 250-400°C, a pressure in the interval 3-25 MPa, and a liquid hourly space

velocity (LHSV) in the interval  $0.5\text{--}8\text{ hr}^{-1}$ , optionally together with intermediate cooling by quenching with cold hydrogen, feed or product. When the objective involves saturation of aromatics the pressure is preferably high, such as 10-25 MPa. The composition of the hydroconversion catalyst actually allows for catalyzing hydrotreatment reactions as well, but according to the present disclosure, it is preferred to separate the exothermal hydrotreatment reactions from the hydroconversion reactions, since too high temperatures in the presence of a hydroconversion catalyst may lead to undesired overcracking and other side reactions, sacrificing yield or catalyst lifetime. Therefore, an upstream hydrotreatment step with complete or close to complete hydrotreatment is commonly preferred. The determination of the exact conditions will require experimental optimization, familiar to the skilled person, involving determination of the severity (by combined optimization of temperature, space velocity, catalyst material and hydrogen pressure) where the boiling point is not substantially changed, while the specific gravity is decreased to the specified range. For production of diesel fuel,  $T_{95}$  of the specification will commonly be  $360^{\circ}\text{C}$  and the specific gravity specification may be 0.81 to 0.96, such that the hydroconversion step (c) of the process receives a hydrotreated hydrocarbon stream having a  $T_{50}$  below  $360^{\circ}\text{C}$  and a specific gravity above 0.96, i.e. a stream which substantially fulfills the boiling point criteria of the diesel specification but not the specific gravity criteria. For production of jet fuel,  $T_{95}$  of the specification will commonly be  $300^{\circ}\text{C}$  and the specific gravity specification may be 0.78 to 0.82, such that the hydroconversion step (c) of the process receives a hydrotreated hydrocarbon stream having a  $T_{50}$  below  $300^{\circ}\text{C}$  and a specific gravity above 0.82, i.e. a stream which substantially fulfills the boiling point criteria of the diesel specification but not the specific gravity criteria. In both cases the hydroconversion process will have a balanced severity, converting a significant amount of aromatic, olefinic and cyclic bonds, without cracking a substantial amount of hydrocarbons to smaller molecules, which will reduce the specific gravity and increase the hydrogen content in ways which may not be obtained by hydrotreatment alone. When the disclosed process is applied to pyrolysis oil from end of life tires, the commercial transportation fuel specification of relevance may mainly be for diesel and marine fuels, since jet and naphtha specifications may require other processes to be fulfilled.

[0034] Since a hydroconversion catalyst inherently also will have hydrotreatment activity, the nomenclature known to the skilled person is emphasized. A hydrotreatment catalyst will not show significant hydroconversion activity and will not contain zeolites, molecular sieves or silica-alumina in catalytically active amounts and the carbon-carbon single-bonds are not affected by contact with a hydrotreatment catalyst. Nevertheless, the molecular structure may be changed during hydrotreatment, e.g. by releasing oxygen atoms defining the molecular structure.

[0035] Similarly, the definition of a hydroconversion catalyst relative to an hydroisomerization catalyst is also appropriate. A hydroisomerization catalyst will inherently have a side reaction activity for hydroconversion. The nature of hydroconversion will involve a consumption of hydrogen, due to the opening of rings and the breakage of hydrocarbons. For the purpose of the present disclosure, a catalytic process shall be considered a hydroisomerization process if at least 50% of the changes of hydrocarbonaceous molecules is made without net addition of hydrogen to the hydrocarbonaceous molecules, contrary to e.g. hydrotreatment replacing heteroatoms with hydrogen without significant modification of and saturating double bonds and aromatic structures or hydroconversion, breaking carbon-carbon bonds by insertion of hydrogen.

[0036] As mentioned, hydroconversion involves breaking of carbon-carbon bonds, and since the boiling point of shorter hydrocarbon molecules is lower than that of longer molecules, hydroconversion involves a loss of high boiling product to lower boiling product. While raw product boiling in the naphtha range (80-150°C), product boiling in the aviation range (150-290°C) and product boiling in the diesel range (150-390°C) may be of similar value, the cracking will involve a shortening of carbon molecules and thus a reduction of the mass of liquid product, with the related result of conversion of liquid transportation fuels to gaseous hydrocarbons of lower value, i.e. a loss of liquid transportation fuel yield. Therefore, hydrocracking of feedstock is carried out on fractions boiling above the desired product range, to minimize this yield loss.

[0037] When the objective of hydroprocessing is traditional hydrocracking to reduce molecular weight and boiling point the feedstock directed to the process is fractionated to contain a minimum boiling below the desired end point, to

minimize loss of liquid product yield. However, if the objective is the conversion of cyclic molecules to branched molecules, with the related effect of shifting the aromatic to non-aromatic cyclic molecule equilibrium away from aromatic molecules, contrary to the objective of reducing molecular weight according to traditional hydrocracking, the stream directed to hydroconversion is instead having a boiling point distribution with a wide overlap with the desired product. An amount of the stream may be boiling at higher temperatures, to compensate for the inevitable reduction of molecular weight, but to have a substantial conversion of cyclic molecules to non-cyclic molecules the stream for hydroconversion must include a fraction overlapping the desired product boiling point range. The addition of hydrogen to the hydrocarbonaceous cyclic molecules has the further advantage of increasing the molecular weight and reducing the density, such that the volume is increased by two mechanisms.

[0038] It is desired to upgrade the middle distillate fraction of the hydrotreated pyrolysis oil to comply with diesel and aviation fuel standards or at least provide a product which is suitable for blending into such products. In addition, the properties of the fraction boiling in the naphtha range are not in compliance with the requirements for use in gasoline. Also for this fraction, the density is above the required level, and in addition, as a consequence of the aromatic nature, the concentration of benzene is also too high. However, where ring opening of middle distillate boiling range products improves the cetane number, the removal of cyclic molecules in naphtha typically decreases the octane number, and thus the value of the product, and therefore the naphtha fraction of the product may typically beneficially be removed from the middle distillate fraction prior to hydroconversion, in order to maximize the value and the volume of this naphtha fraction. The naphtha fraction also has several possible applications, e.g. as a gasoline fraction, as a source for extraction of aromatics; benzene, toluene and xylenes, as paraffinic naphtha for use in steam crackers after hydroconversion or finally the naphtha fraction and light gases it may also be directed for use in hydrogen production, and in this case, the cost of fractionation prior to hydroconversion may not be justified.

[0039] A hydroprocessed stream comprising hydrocarbons, excess hydrogen and inorganic molecules comprising heteroatoms must be separated in hydrocarbons

and molecules comprising heteroatoms, which – typically are gaseous. To do this, the hydroprocessed stream is directed to a separation section, which for process scenarios relating to the treatment of pyrolysis oil typically either will be between a base metal based hydrotreatment reactor and a noble metal based hydroconversion reactor, or if the hydroconversion catalyst comprises base metals, downstream the hydroconversion reactor. The process may also comprise one or more other conversion steps, such as hydroconversion or hydroisomerization, and depending on the sequence of these steps and the catalytically active metals used, the skilled person will be aware of the possible positions for introducing a separation section with the purpose of withdrawing a recycle gas stream.

[0040] As the development of heat and the consumption of hydrogen is high in processes treating feedstocks rich in oxygenates, the gas to oil ratio in the hydroprocessing reactors is also very high compared to other hydroprocessing processes, such as from 1000 to 7000 Nm<sup>3</sup>/m<sup>3</sup>. This hydrogen gas may be used to control process temperatures, by stepwise injections of cooled gas. Typically the gas to oil ratio is selected from the hydrogen concentration in the treat gas and the expected consumption of hydrogen, as calculated from the molecular composition of the feedstock, including the average number of double bonds and aromatic bonds, heteroatoms and the expected breaking of carbon-carbon bonds, multiplied by a safety factor which may be from 2 to 10 times, dependent on the nature of the process, including the risk of process runaway.

[0041] The pyrolysis oil product streams may contain aromatic hydrocarbons, long linear hydrocarbons, gaseous hydrocarbons, water and to some extent carbon oxides. In addition nitrogen and chloride in the hydrocarbonaceous feedstock will result in ammonia and hydrogen chloride in the hydroprocessed stream; which may solidify as ammonium chloride. Added sulfur as well as any sulfur in the pyrolysis oil will be present as hydrogen sulfide in the hydroprocessed stream, and finally an excess amount of hydrogen will pass unreacted to the hydroprocessed stream. Intermediate separation steps may be required for optimal handling of this diverse mixture, so especially if some process steps are carried out using a catalyst comprising noble metals, “sour gases”, including H<sub>2</sub>S, CO<sub>2</sub> and NH<sub>3</sub>, are removed prior to these reactions.

[0042] In addition, the necessity to combine 3 or 4 catalysts for optimal conversion of pyrolysis oil into hydrocarbons naturally complicates the process layout, and the sequence of the materials must be considered carefully, especially concerning the presence of sulfur required for base metals and shunned for noble metals.

[0043] In the process layouts, recycle may be used for different purposes; gas recycle for efficient use of hydrogen, liquid recycle around the hydroconversion catalyst to maximize the yield of the desired fraction and liquid recycle around the hydrotreatment catalyst to limit the temperature increase due to exothermal deoxygenation reactions as well as to limit the reaction rate of polymerization reactions for reactive oxygenates and other reactive compounds in the pyrolysis oil. The choice of recycle configuration will be related to different benefits, including process simplicity by minimizing the number of recycle loops, minimizing reactor volume and cost by choosing configurations with low recycle volumes, maximizing process reactivity control by high recycle volume and/or extensive cooling, and minimizing polymerization by high recycle volume.

[0044] Process configurations without recycle may also be beneficial due to simplicity and low cost, especially in the cases where the process volume is moderate, or where an appropriate diluent is available.

## Description of Drawings

[0045] Figure 1 shows a process for conversion of solid material to transportation fuel. A solid feedstock (2) such as end of life tires or ligneous waste (straw, wood or similar) is directed to a hydrothermal decomposition plant (PYP), which may be of several different types. In the illustration, solids (4) such as char and carbon black, pyrolysis gas (6) and pyrolysis oil (8) are released from the hydrothermal decomposition plant (PYP), but not all fractions may be present. Commonly the pyrolysis oil is only formed after cooling a vapor phase from the pyrolysis process. In addition to pyrolysis oil, water may also be condensed from the vapor phase. Integrated in the pyrolysis process, a hydrotreatment process may also be carried out in which the pyrolysis vapor or the pyrolysis oil is contacted with hydrogen in the presence of a hydrotreatment catalyst, e.g. in a process where the catalyst is fluidized. A step of hydrotreatment (HDT) is carried out in order to provide a hydrotreated intermediate after combination of a hydrogen rich stream (10) and the pyrolysis oil (8), in the presence of a hydrotreatment catalyst (HDT)



comprising one or more metals typically sulfided base metals, but possibly noble metals, on a refractory support such as alumina. Here this step is shown as a single fixed bed reactor (HDT), but the step may in practice involve multiple reactors, local recycle of intermediate product, splitting of the feed between multiple and other variations known e.g. from the treatment of renewable fats and oils and/or fossil feedstocks.

[0046] The hydrotreated intermediate (12) is directed to a first fractionation step (FRAC1), in which gas (14), naphtha (16), diesel (17) and high boiling hydrotreated hydrocarbons (18) are separated, and the diesel (17) and the high boiling hydrotreated hydrocarbon (18) are combined with a recycle heavy product (20) and directed as a stream for hydroconversion (22) to further hydroprocessing in a hydroconversion reactor (HC), where it contacts a hydroconversion catalyst, comprising an active metal, which may either be a sulfided base metal or a noble metal, and an acidic support, such as a zeolite. The hydroconversion produces a hydroconverted hydrocarbon stream (24), by saturating aromatics and breaking carbon-carbon bond to open hydrocarbon rings, with a side effect of reducing molecular weight by cleaving some molecules. Accordingly, the amount of cyclic compounds is reduced and the boiling point range of the hydroconverted hydrocarbon stream (24) is changed with a reduction of the amount of middle distillate, such as jet and diesel, and a provision of naphtha and fuel gases, which are separated in a second fractionation step (FRAC2), into gas (26), naphtha (28), diesel (30) and recycle heavy product (20). The naphtha produced during hydroconversion (28) will be paraffinic and thus have a lower octane number, and may therefore be preferred to be directed to a hydrogen plant, to provide the hydrogen for the process. Since the high boiling hydrotreated hydrocarbons (18) were fractionated to include an amount boiling above the middle distillate boiling range, an amount of such heavy product is likely to be present for recycle to the inlet of the hydroconversion reactor.

[0047] Fig.1 was made to illustrate the principles of the process, and for simplicity details have been omitted, including heat exchangers, the gas loop and phase separators.

[0048] In an alternative embodiment, the entire hydrotreated intermediate (12) may in combination with the recycle heavy product (20) be directed as the stream for hydroconversion (24).

## Description of Embodiments

[0049] Multiple aspects of the disclosed invention exists.

[0050] A first aspect of the present disclosure relates to a process for production of a hydrocarbon composition useful as a transportation fuel according to a commercial transportation fuel specification from a hydrocarbonaceous feedstock comprising at least 0.5 wt% oxygen and at least 25 wt% carbon in cyclic structures, comprising the steps of

- a. directing a hydrocarbonaceous feedstock to hydrotreatment in one or more steps providing an intermediate product comprising less than 0.1 wt% oxygen and a specific gravity, for the fraction boiling in the range defined by the commercial transportation fuel specification, above the upper limit of specific gravity under the commercial transportation fuel specification,
- b. providing a hydrotreated hydrocarbon stream for hydroconversion from said intermediate product optionally by fractionation, wherein said fraction for hydroconversion has a  $T_{50}$  being below  $T_{95}$  of the commercial transportation fuel specification,
- c. directing the stream for hydroconversion to contact a hydroconversion catalyst under hydroconversion conditions to provide a hydroconverted hydrocarbon stream,
- d. fractionating said hydroconverted hydrocarbon stream to provide at least said hydrocarbon composition useful as a transportation fuel.

[0051] This has the associated benefit of providing a cost effective process for production of transportation fuels from a cyclic aromatic feedstock.

[0052] A second aspect of the process according to the first aspect, wherein fractionating said hydroconverted hydrocarbon stream further provides at least a fraction boiling above  $T_{95}$  of the commercial transportation fuel fuel specification,

which is directed as recycle to be combined with said hydrotreated hydrocarbon stream for hydroconversion.

[0053] This has the associated benefit of also converting high boiling feedstock to transportation fuel.

[0054] A third aspect of the process according to the first or second aspects, wherein the hydroconversion conditions involves a pressure above 15 MPa and below 25 MPa.

[0055] This has the associated benefit of such elevated pressure favoring addition of hydrogen for saturation of aromatics and opening of cyclic structures.

[0056] A fourth aspect of the process according to any aspect above, wherein the hydroconversion conditions involves a temperature above 350°C and below 420°C.

[0057] This has the associated benefit of providing severe conditions, supporting high reactivity.

[0058] A fifth aspect of the process according to any aspect above, wherein the hydroconversion catalyst comprises an active metal, either one or more elemental noble metals such as platinum and/or palladium or one or more sulfided base metals such as nickel, cobalt, tungsten or molybdenum, an acidic support, such as a molecular sieve showing high activity in breaking carbon-carbon bonds, and having a topology such as MFI, BEA and FAU or amorphous silica-alumina and optionally a refractory support such as alumina, silica or titania, or combinations thereof.

[0059] This has the associated benefit of such a material being active in hydroconversion reactions, where the carbon-carbon bonds are broken and molecular structure is changed.

[0060] A sixth aspect of the process according to any aspect above, wherein at least one step of hydrotreatment is carried out outside a fixed bed reactor.

[0061] This has the associated benefit of enabling a process of hydrotreatment in close coupling with an upstream thermochemical conversion process.

[0062] A seventh aspect of the process according to any aspect above, wherein at said commercial transportation fuel specification is a diesel specification, such as European Standard, EN590.

[0063] This has the associated benefit of a diesel fuel having a large overlap of boiling point range with a feedstock originating from thermochemical conversion.

[0064] An eighth aspect of the process according to any aspect above, wherein the provision of a hydrotreated hydrocarbon stream for hydroconversion from said intermediate product by fractionation involves separating said intermediate product into a fraction boiling in the naphtha range and a fraction boiling above the naphtha range.

[0065] This has the associated benefit of enabling avoiding hydroconversion of the fraction boiling in the naphtha range, which would reduce the octane number of this fraction.

[0066] A ninth aspect of the process according to any aspect above, wherein the hydrocarbonaceous feedstock originates from a thermochemical decomposition process.

[0067] This has the associated benefit of enabling upgrading of such a hydrocarbonaceous feedstock from a thermochemical decomposition process, which may be especially useful if it comprises high amounts of cyclic structures from the material directed to the thermochemical decomposition process, as would be the case from end of life tires and ligneous materials.

[0068] An additional aspect of the invention relates to a process plant for production of a hydrocarbon by a process according to any aspect above.

## Examples

[0069] A process illustrating Figure 1 is evaluated with basis in experiments, in combination with evaluations of process simulations.

[0070] Case 1 illustrated in Table 1 represents the process layout according to Figure 1, but taking out heavy product 20 instead of recycling it, for simplicity. Here a pyrolysis oil originating from pyrolysis of end of life tires (stream 8) is hydrotreated, separated in naphtha and a higher boiling fraction and directed to contact a hydroconversion catalyst under conditions resulting in a diesel product

comprising a low amount of aromatics and a specific gravity value in compliance with EN590 requirements (0.8391 vs. the specified 0.845). The severity of the conditions is illustrated by the conversion of the fraction boiling above 390°C, of which 73.5 wt% is converted to lower boiling product.

[0071] Stream 16 is a fraction of aromatic naphtha corresponding to 15 wt%FF (wt% on fresh feed basis). In addition, 16 wt%FF naphtha with 8.3 wt% aromatics is produced in stream 28, and in stream 30 62 wt%FF diesel with 4.0 wt% aromatics is produced. In addition, 6.1 wt%FF is available as unconverted oil, which could be directed as recycle.

[0072] Case 2 illustrated in Table 2 similarly represents a variant of the process layout according to Figure 1 in which all of the hydrotreated product 12 is directed to hydrocracking. The severity of the conditions is illustrated by the conversion of the fraction boiling above 390°C. In this case 56.5 wt% is converted to lower boiling product. For practical reasons the experiments were carried out with only the liquid fraction of the hydrotreated product 12 being directed to hydrocracking.

[0073] Here 66 wt%FF diesel is produced, which has a specific gravity slightly above the EN590 requirements (0.8468 vs. the specified 0.845). Even if slightly more severe conditions were chosen, the diesel yield would be expected to be around 64 wt%FF, i.e. slightly above that shown in Table 1.

[0074] With respect to naphtha only 24 wt% FF is produced, with 13 wt% aromatics, which is about half the amount, with a low aromatics content.

[0075] Finally, case 3 illustrated in Table 3 represents a situation where the intermediate fractionation provides naphtha and diesel and hydroconversion is operated as hydrocracking in order to maximize liquid yields. This case shows a total of 76.5 wt% diesel and 18.1 wt% naphtha, which is slightly higher combined yield of product boiling in the diesel and naphtha ranges compared to case 1 or 2, but the 62 wt% FF diesel product does not fulfill specific gravity specifications, and will therefore introduce limitations on use, even in blends.

[0076] In summary, the results show that for case 1, with hydroconversion of the fraction boiling in the diesel range and above, a fraction of diesel is provided in compliance with specific gravity requirements. In addition, two naphtha streams

are provided; one with high aromatic content (and thus high octane number) and one with low aromatic content.

[0077] For case 2, the amount and quality of the diesel fraction is above that of case 1, but only a single naphtha fraction is provided. The naphtha has a low content of aromatics, and the quantity is below that of case 1.

[0078] For case 3, it is seen that a higher amount of diesel and naphtha may be obtained, but that the diesel fraction has very poor specific gravity value, and thus only has a limited value as diesel blendstock. Furthermore, the density being almost 4% above the specification also has the consequence that the volume for the same mass is 4% lower, so the loss of mass is to some extent compensated by an increase of volume.

**Table 1**

		8	12	16	18	24	28	30	20
C1-4	[wt% FF]	0	1.1			2.0			
C5-150°C	[wt% FF]	13	15	15		16	16		
150-390°C	[wt% FF]	55	62		85	62		62	
>390°C	[wt% FF]	32	23			6.1			6.1
Aromatics	[wt%]	49	35	41	27	4.1	8.3	4.0	3.6
Naphthenes	[wt%]	3.6	38	43	29	36	72	35	31
Oxygen	[wt%]	1.2	ND	ND	ND	ND	ND	ND	ND
SG		0.9348	0.8808	0.7941	0.8955	0.8290	0.7624	0.8391	0.8855

**Table 2**

		8	12	24	28	30	20
C1-4	[wt% FF]	0	1.1	1.5			
C5-150	[wt% FF]	13	15	24	24		
150-390	[wt% FF]	55	62	66		66	
>390	[wt% FF]	32	23	10			10
Aromatics	[wt%]	49	35	7.0	13	7.0	3.4
Naphthenes	[wt%]	3.6	38	38	71	38	19
Oxygen	[wt%]	1.2	ND	ND	ND	ND	ND
SG		0.9348	0.8808	0.8346	0.7704	0.8468	0.8988

**Table 3**

		8	12	16	17	18	24	28	30	20
C1-4	[wt% FF]	0	1.1				1.0			
C5-150	[wt% FF]	13	15	15			3.1	3.1		
150-390	[wt% FF]	55	62		62		14.5		14.5	
>390	[wt% FF]	32	23			23	2.3			2.3
Aromatics	[wt%]	49	35	41	32	39	2.6	5	2	3.2
Naphthenes	[wt%]	3.6	38	43	38	35	40	75	35	25
Oxygen	[wt%]	1.2	ND	ND	ND	ND	ND	ND	ND	ND
SG		0.9348	0.8808	0.7941	0.8780	0.9530	0.8350	0.7700	0.8450	0.8750

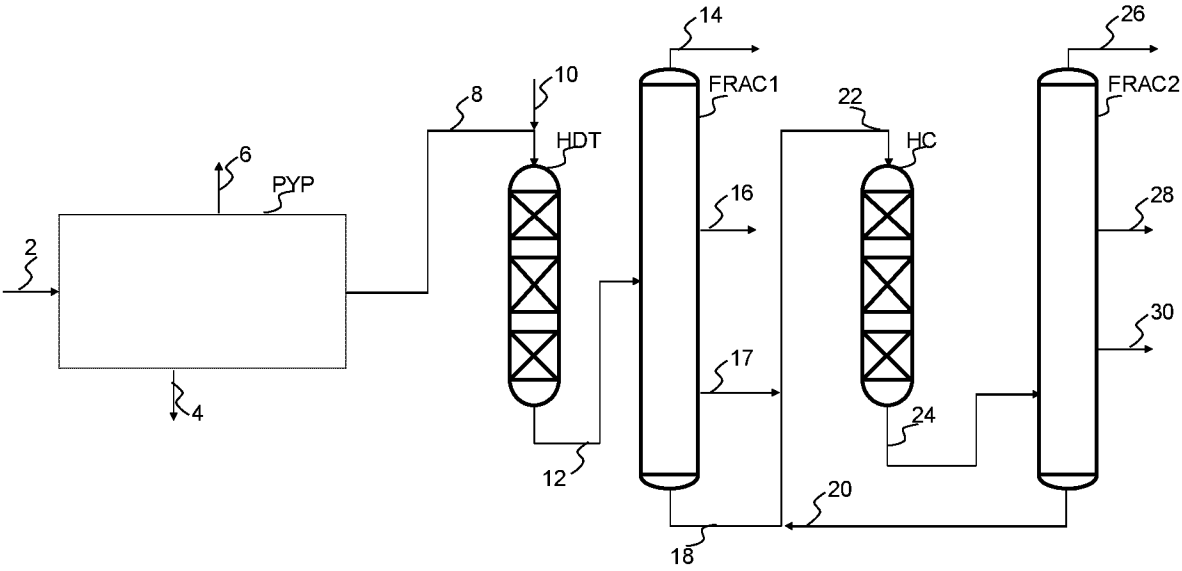
## Claims

- [Claim 1] A process for production of a hydrocarbon composition useful as a transportation fuel according to a commercial transportation fuel specification from a hydrocarbonaceous feedstock comprising at least 0.5 wt% oxygen and at least 25 wt% carbon in cyclic structures, comprising the steps of
- directing a hydrocarbonaceous feedstock to hydrotreatment in one or more steps providing an intermediate product comprising less than 0.1 wt% oxygen and a specific gravity, for the fraction boiling in the range defined by the commercial transportation fuel specification, above the upper limit of specific gravity under the commercial transportation fuel specification,
  - providing a hydrotreated hydrocarbon stream for hydroconversion from said intermediate product optionally by fractionation, wherein said fraction for hydroconversion has a  $T_{50}$  being below  $T_{95}$  of the commercial transportation fuel specification,
  - directing the stream for hydroconversion to contact a hydroconversion catalyst under hydroconversion conditions to provide a hydroconverted hydrocarbon stream,
  - fractionating said hydroconverted hydrocarbon stream to provide at least said hydrocarbon composition useful as a transportation fuel.
- [Claim 2] A process according to claim 1, wherein fractionating said hydroconverted hydrocarbon stream further provides at least a fraction boiling above  $T_{95}$  of the commercial transportation fuel specification, which is directed as recycle to be combined with said hydrotreated hydrocarbon stream for hydroconversion.
- [Claim 3] A process according to claim 1 or 2, wherein the hydroconversion conditions involves a pressure above 15 MPa and below 25 MPa.
- [Claim 4] A process according to claim 1, 2 or 3, wherein the hydroconversion conditions involves a temperature above 350°C and below 420°C.



- [Claim 5] A process according to claim 1, 2, 3 or 4, wherein the hydroconversion catalyst comprises an active metal, either one or more elemental noble metals such as platinum and/or palladium or one or more sulfided base metals such as nickel, cobalt, tungsten or molybdenum, an acidic support, such as a molecular sieve showing high activity in breaking carbon-carbon bonds, and having a topology such as MFI, BEA and FAU or amorphous silica-alumina and optionally a refractory support such as alumina, silica or titania, or combinations thereof.
- [Claim 6] A process according to claim 1, 2, 3, 4 or 5, wherein at least one step of hydrotreatment is carried outside a fixed bed reactor.
- [Claim 7] A process according to claim 1, 2, 3, 4, 5 or 6, wherein at said commercial transportation fuel specification is a diesel specification, such as European Standard, EN590.
- [Claim 8] A process according to claim 1, 2, 3, 4, 5, 6 or 7 wherein the provision of a hydrotreated hydrocarbon stream for hydroconversion from said intermediate product by fractionation involves separating said intermediate product into a fraction boiling in the naphtha range and a fraction boiling above the naphtha range.
- [Claim 9] A process according to claim 1, 2, 3, 4, 5, 6, 7 or 8 wherein the hydrocarbonaceous feedstock originates from a thermochemical decomposition process.
- [Claim 10] A process plant for production of a hydrocarbon by a process according to claim 1, 2, 3, 4, 5, 6, 7, 8 or 9.

[Fig. 1]



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2023/058325

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> <b>INV.</b> C10B53/02 C10G1/10 C10G1/00 C10G3/00 C10G47/16 C10G65/12 C10G69/06 <b>ADD.</b> According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) <b>C10B C10H C10G</b>  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) <b>EPO-Internal, WPI Data</b>		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<b>US 2021/395620 A1 (ANDERSSON ASBJØRN SUNE [DK] ET AL) 23 December 2021 (2021-12-23) figures 1-3 paragraphs [0032], [0035], [0037], [0066]</b> -----	1-10
X	<b>US 2012/151828 A1 (KALNES TOM N [US]) 21 June 2012 (2012-06-21) figure 1 paragraphs [0031], [0056]</b> -----	1-10
X	<b>US 2009/287029 A1 (ANUMAKONDA AMARENDRA [US] ET AL) 19 November 2009 (2009-11-19) figure 1 paragraph [0015]</b> -----	1-10
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed  "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art  "&" document member of the same patent family		
Date of the actual completion of the international search  <b>20 April 2023</b>		Date of mailing of the international search report  <b>03/05/2023</b>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  <b>Ruiz Martínez, C</b>

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