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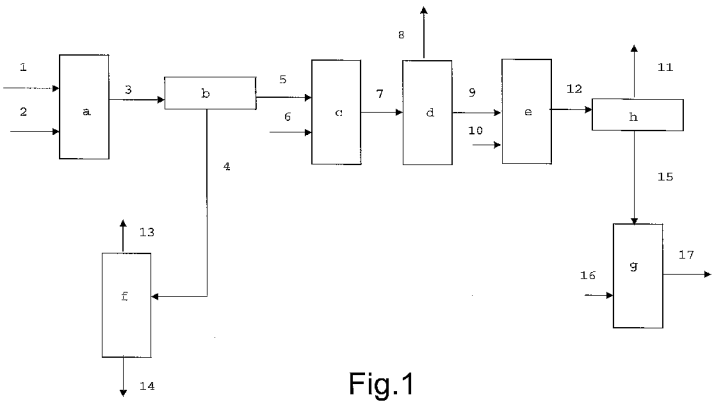

Fig.1

(57) Abstract: A process is described for the production of hydrocarbon fractions which can be used as diesel fuel or as components of diesel fuel, starting from a mixture of a biological origin containing fatty acid esters with glycerine, and possibly containing aliquots of free fatty acids and/or phosphoglycerides, wherein said process comprises the following steps: - subjecting the mixture of a biological origin to hydrolysis, obtaining a mixture containing glycerine and a mixture of fatty acids, - neutralizing the mixture of fatty acids with ammonia, - subjecting the neutralized mixture to hydrodeoxygenation, - subjecting the mixture resulting from the hydrodeoxygenation to hydroisomerization. The process of the present invention allows the triglycerides. This aspect, in addition to allowing the recovery of glycerine, which can be used as precursor of fuel components, allows the hydrogen consumption to be avoided in the hydrodeoxygenation step, which occurs when glycerine is present and therefore undergoes reduction to propane. Furthermore, if the mixture of a biological origin also contains aliquots of free fatty acids, the process of the invention also avoids problems of corrosion due to said acids, during the hydrodeoxygenation treatment.

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PROCESS FOR THE PRODUCTION OF HYDROCARBON FRACTIONS FROM MIXTURES OF A BIOLOGICAL ORIGIN

The present invention relates to a process for the production of hydrocarbon fractions which can be used as diesel fuel or as components of diesel fuel, starting from a mixture of a biological origin containing esters of fatty acids with glycerine, and possibly containing aliquots of free fatty acids. The process comprises at least one hydrolysis step, a neutralization step, a hydrodeoxygenation step and a hydroisomerization step, and allows the quantitative recovery of glycerol which can then be used as oxygenated component of fuels.

The use of vegetable oils in diesel engines dates back to Rudolf Diesel who, in 1900, demonstrated the capacity of diesel engines of functioning with peanut oil. During the second world war in Africa, both palm oil and peanut oil were used as fuel for military vehicles. After the war, the technological development led to an almost exclusive use of fuels deriving from oil; diesel engines were also enormously improved, above all with respect to the injectors and control systems, to such an extent that there was little flexibility for the use of fuels different from gasoil. At the same time, vegetable fuels were progressively abandoned due to the high production cost and inconstancy in the product quality.

During the oil crisis of the seventies', attention was refocused on the use of vegetable oils as diesel fuels, but this proved to be difficult for various reasons (formation of crusting in the internal

combustion chamber, blockage of the injectors, dilution of the lubricant). Research activities were therefore directed towards the preparation, starting from vegetable oils, of methyl or ethyl esters and their use in diesel engines. Methyl and ethyl esters of fatty acids are obtained from vegetable oils by transesterification with methanol or ethanol. An alternative approach for the conversion of vegetable oils was proposed in the eighties' and consists in their deep hydrogenation to produce hydrocarbon fractions with a boiling point compatible with diesel fuels obtained from oil. The deep hydrogenation of vegetable oils causes the removal of oxygen with the contemporaneous formation of a mixture of H_2O, CO_2 and CO, in reciprocal ratios varying according to the operative conditions. The starting ester is thus prevalently transformed into hydrocarbons with respect to both the fatty acids and glycerol. Small quantities of free alcohols can be formed together with the hydrocarbons.

The deep hydrogenation reaction of fatty oils for producing liquid fuels was studied for example, again in the eighties', by Nunes et al., who, in the article entitled "Hydrocraquage sous pression d'une huile de soja: procédé d'étude et allure générale de la transformation" (Rev. Inst. Fr. Pet. Of 1086, vol. 41, page 421 onwards) describe the hydrocracking of soybean oil with a bifunctional catalyst. At a temperature higher than 673 K, decarbonylation and decarboxylation of the fatty acids are observed, together with a strong hydrogenolysis due to the presence of the metallic catalyst. The main products are linear-chain

hydrocarbons.

J. Gusmao et al. (Utilization of vegetal oils as an alternative source for diesel-type fuel: hydrocracking on reduced Ni/SiO_2 and sulphided $Ni-Mo/Al_2O_3$, Catalysis Today, vol. 5 of 1989, pages 533 onwards) demonstrates how, in the hydrogenation of soybean oil, the hydrocarbon fraction obtained mainly consists of linear paraffins (96% molar of C_{15} – C_{16} – C_{17} – C_{18}).

US patent 4,992,605 describes a process for producing hydrocarbon fractions in the C_{15}-C_{18} range by the hydrogenation of vegetable oils such as sunflower oil, rape oil, canola oil, palm oil, or fatty oils contained in the pulp of pine trees (tall oil). This hydrocarbon fraction prevalently consists of linear paraffins (C_{15}-C_{18}) and is characterized by a high cetane number, which is such that it can be used as a cetane improver.

In "Hydroprocessed vegetable oils for diesel fuel improvement", Bioresources Technology 56 (1996), pages 13 to 18, the application described in US 4,992,605 is summarized, on a laboratory scale in order to produce a hydrogenated product starting from canola oil. The hydrocarbon fraction almost exclusively consists of linear paraffins and the fraction which distills within the distillation range of diesel fuel, has a cetane number ranging from 55 to 90. Other hydrogenation products include light C_1-C_5 hydrocarbons, water and CO_2. The diesel fraction is defined as "super cetane". The density (0.790 g/ml) is compatible with diesel fuel, whereas the viscosity is slightly higher. The real limit of this fraction, however, is linked to the poor cold properties (cloud and pour points) associated

with the linearity of the paraffins, which exceed 20°C. For this reason, the "super cetane" fraction can be used in a mixture with conventional diesel but not during the winter months.

EP 1396531 describes a process for the production of hydrocarbon components from mixtures of a vegetable or animal origin. The formation of a mixture with a content of iso-paraffins of 73%, is described. The process comprises a pre-hydrogenation step, a hydrodeoxygenation step (HDO) and an isomerization step which operates using the countercurrent flow principle. The pre-hydrogenation step, which is carried out under mild conditions, is necessary for saturating the double bonds present and avoiding undesired side-reactions in the subsequent process steps. In the isomerization step, it is absolutely indispensable to operate in countercurrent to protect the catalyst from deactivation caused by the water contained in the feeding deriving from the previous HDO step: when operating in countercurrent, part of the water contained in the hydrocarbon feeding is removed, before said feeding comes into contact with the whole catalyst of the catalytic bed.

Patent application WO2008/058664 describes a process for producing hydrocarbon fractions which can be used as diesel fuel starting from a mixture of a biological origin, containing fatty acid esters, possibly with aliquots of free fatty acids, by means of a process which comprises the following steps:

(1) hydrodeoxygenation of the mixture of a biological origin;

(2) hydroisomerization of the mixture resulting from

step (1), after a possible purification treatment, said hydroisomerization being effected in the presence of a catalytic system which comprises:

a) a carrier of an acid nature comprising a micro-mesoporous silico-alumina completely amorphous, having a SiO_2/Al_2O_3 molar ratio ranging from 30 to 500, a surface area greater than 500 m^2/m, a pore volume ranging from 0.3 to 1.3 ml/g, an average pore diameter lower than 40 Å,

b) a metal component containing one or more metals of group VIII, possibly in a mixture with one or more metals of group VIB.

In US 7,999,143, a feedstock consisting of triglycerides of an animal or vegetable origin, after a pre-treatment and purification section, is fed to a hydrodeoxygenation reactor. In this section, the feedstock is deoxygenated by dehydrogenation, the glycerine component is transformed to propane and the component deriving from the fatty acid of the triglyceride is transformed to a paraffin having a number of carbon atoms equal to that of the starting fatty acid. The heavy n-paraffins are separated and sent to an isomerization step to convert part of the n-paraffins to iso-paraffins, thus allowing an improvement in the flow properties at low temperatures, necessary for using this paraffin mixture as bio-component for diesel gasoils or jet-fuel.

In the processes described above, the starting feedstocks frequently contain variable concentrations of free acids. The presence of free acids can cause serious problems of corrosion, thus requiring the use

of an expensive and special metallurgy for the construction of different sections of the plant. Various measures are adopted for avoiding this increase in costs, such as the separation and removal of the free acids, or the separation of the fatty acids and reaction of the same with glycerine to form further triglycerides which can be added to the process. The problem of the free fatty acids, however, has other implications of greater importance. Numerous studies have in fact been underway for some years now, aimed at the growth of microalgae destined for the production of bio-oil for bio-diesel: a relevant quantity of lipids is contained in the cell walls of many algal strains in the form of phospholipids, in particular, phosphoglycerides and consequently, in order to recover all of the oily phase available in the algal bio-mass, it is necessary to effect the hydrolysis of the phospholipids, particularly phosphoglycerides, wherein said process inevitably also leads to the hydrolysis of part of the triglycerides. For this reason, the production of bio-oil from algal biomass leads to the production of bio-oil containing extremely high concentrations of free acids, and even to the production of mixtures of fatty acids. This is why the production of bio-oil from algae makes the use of corrosion-prevention strategies even more important.

US 8,440,875 describes the possibility of neutralizing the component of free fatty acids present in the mixture of triglycerides by the addition of ammonia, in order to form ammonium salts of free acids. The mixture of triglycerides and ammonium salts of fatty acids is then subjected to deoxygenation: during

the reaction, n-paraffins are formed, corresponding to the aliphatic chains of triglycerides, with the formation of water, carbon dioxide and carbon monoxide, whereas the ammonium ion is re-transformed into ammonia which is separated by a scrubber downstream of the deoxygenation reactor and upstream of the isomerization reactor. This solution allows the problem of corrosion to be faced within a traditional hydrodeoxygenation scheme and possible isomerization of mixtures of glycerides, i.e. mixtures of mono- di- and tri-esters of fatty acids with glycerine, containing aliquots of free fatty acids: this solution leads to the formation of paraffins suitable for being used as fuels, but causes the loss of glycerine which is transformed to propane during the hydrodeoxygenation step, with the consequent useless consumption of hydrogen.

The problem relating to the loss of glycerine esterified with fatty acids in the mixtures of triglycerides, therefore remains unsolved; as mentioned above, in fact, in the production of hydrocarbons from triglycerides by deoxygenation, the aliquot of glycerine contained in the triglycerides is hydrogenated to propane: it is therefore subtracted from its possible use in the production of liquid energy vectors, generating, on the other hand, a gaseous energy vector, bio-LPG.

As described, for example, in patent application WO2013150457, glycerine can, on the contrary, be conveniently used for the production of oxygenated components for fuels which, depending on their nature, can be used as bio-components for gasolines or for diesel. In particular, WO2013150457 describes fuel

compositions containing:

- a hydrocarbon mixture
- at least one ketal or cyclic acetal,

wherein said ketals and acetals are obtained by the reaction of a diol with a carbonyl compound, wherein said diol is prepared starting from glycerine.

EP 1321502 describes a composition comprising gasoil and particular acetals of glycerine.

In C.J.A. Mota et al. Energy Fuels 2010, 24, 2733-2736, reaction products of glycerine with acetone and formaldehyde are used as additives for gasolines.

In J.F. Izquierdo et al., Renewable and Sustainable Energy Reviews 16 (2012) 6717-6724, the etherification reaction of glycerine with light olefins is described, in order to obtain additives for diesel and bio-diesel.

WO2009/115273 describes a process for preparing ethers of glycerine which can be used as oxygenated components for fuels: the process comprises the reaction of glycerine with a linear olefin selected from 1-butene, 2-butene, 1-pentene, 2-pentene, and mixtures thereof, in the presence of a strong acid catalyst, at a temperature ranging from 80 to 180°C.

Bio-components for diesel are particularly valuable for a combined use with hydrogenated vegetable oil (HVO) as they correct the low density of HVO and the presence of oxygen also reduces the particulate emissions from diesel engines.

It also appears evident that, for mixtures of a biological origin deriving from oils and animal or vegetable fats, and therefore particularly for oils deriving from micro-algae, there are generally management problems of the part of the plant relating

to hydrodeoxygenation, and the necessity is consequently strongly felt for finding methods which allow the exploitation of mixtures of a biological origin containing triglycerides, particularly algal biomasses, which do not require a costly and special metallurgy for the construction of the parts of the plant relating to the hydrodeoxygenation reaction.

A new process has now been found for the production of hydrocarbon mixtures from mixtures of a biological origin containing fatty acid esters with glycerine, and possibly free fatty acids; the new process allows the co-production of glycerine, which can be destined for the use of oxygenated bio-components for fuels, and does not have, during the hydrodeoxygenation step, problems of corrosion due to the presence of free fatty acids. Said process consumes a smaller quantity of hydrogen due to the fact that, as the glycerine is removed from the reaction environment before coming into contact with the hydrogen, it does not undergo reduction reactions to propane.

An object of the present invention therefore relates to a process for the production of hydrocarbon mixtures which can be used as diesel fuel or diesel fuel components, starting from a mixture of a biological origin containing fatty acid esters with glycerine, and possibly containing free fatty acids and/or phosphoglycerides, which comprises the following steps:

- subjecting the mixture of a biological origin to hydrolysis, obtaining a mixture containing glycerine and containing a mixture of fatty acids,
- neutralizing the mixture of fatty acids with

ammonia,

- subjecting the neutralized mixture to hydrodeoxygenation,
- subjecting the mixture resulting from the hydrodeoxygenation to hydroisomerization.

According to a preferred aspect, the process of the present invention comprises the following steps:

1) subjecting the mixture of a biological origin to hydrolysis, obtaining a mixture containing the corresponding fatty acids and glycerine,
2) separating the glycerine from the mixture of fatty acids,
3) neutralizing the mixture of fatty acids with ammonia, obtaining the corresponding ammonium salts,
4) subjecting the mixture of ammonium salts to hydrodeoxygenation obtaining ammonia and a mixture containing paraffins,
5) separating the ammonia from the mixture containing paraffins,
6) subjecting the mixture containing paraffins to hydroisomerization.

The process of the present invention therefore comprises a hydrolysis step of fatty acid esters with glycerine, possibly containing aliquots of free fatty acids and/or phosphoglycerides, with the transformation of said esters into the corresponding free fatty acids and glycerine, which can then be destined for the production of oxygenated bio-components.

The mixture of a biological origin used in the process of the present invention can contain fatty acid esters with glycerine, and can possibly additionally

contain free fatty acids or phosphoglycerides, or the mixture of a biological origin can contain, in addition to fatty acid esters with glycerine, both free fatty acids and phosphoglycerides.

The phosphoglycerides can be present for example in the case of mixtures of a biological origin deriving from microalgae.

In the particular case in which a mixture of a biological origin containing fatty acid esters, phosphoglycerides, and possibly free fatty acids, is subjected to hydrolysis, glycerine, a mixture of fatty acids and phosphoric acid is obtained.

The mixtures of a biological origin used in the process of the present invention can be mixtures of a vegetable or animal origin. Said mixtures contain fatty acid esters with glycerine selected from mono- di- and tri-esters and mixtures thereof, and prevalently contain tri-esters. Said esters are also indicated with the name of glycerides, in particular mono- di- and tri-glycerides. The fatty acid esters typically contained in said mixtures are therefore mainly triglycerides of fatty acids, in which the hydrocarbon chain of the fatty acid can contain from 12 to 24 carbon atoms and can be mono- or poly-unsaturated. The mixtures of a biological origin can be selected from vegetable oils, vegetable fats, animal fats, fish oils or mixtures thereof. Vegetable oils or fats can be sunflower oil, rape oil, canola oil, palm oil, soybean oil, hemp oil, olive oil, linseed oil, peanut oil, castor oil, mustard oil, coconut oil or fatty oils contained in the pulp of pine trees (tall oil), or mixtures thereof. Animal oils or fats can be selected

from lard, suet, tallow, milk fats, and mixtures thereof. Recycled oils or fats of the food industry, of both an animal and vegetable origin, can also be used. The vegetable oils or fats can also derive from plants selected by means of genetic manipulation.

All of the oils or fats mentioned above can contain an aliquot of fatty acids: when present, said aliquot can generally range from over 0 to 30% by weight with respect to the total mixture of a biological origin.

In the particular case of mixtures of a biological origin deriving from microalgae, the aliquot of free fatty acids can also be higher. A high quantity of lipids is in fact contained in the cell walls of microalgae in the form of phospholipids, in particular phosphoglycerides, whose recovery requires the hydrolysis of the phospholipids, which necessarily also determines, at least in part, the hydrolysis of the triglycerides. The resulting bio-oil therefore contains a high concentration of free acids, which can reach up to 60%.

In the hydrolysis step of the mono-, di- and tri-esters of fatty acids with glycerine, contained in the mixture of a biological origin, their transformation to acids and glycerine is obtained: the hydrolysis is carried out by operating in the presence of water, preferably water containing a base.

The base is preferably selected from ammonia, ethanolamine, aliphatic amines. The amines are preferably mono-alkyl-amines, even more preferably mono-alkyl-amines containing from 1 to 5 carbon atoms, particularly ethylamine or propylamine.

A particularly preferred aspect is to use ammonia.

The base is preferably used in a quantity which ranges from 0.1/1 to 4/1 moles with respect to the moles of fatty acid esters with glycerine.

Small percentages of salts of acids with the base used can be formed during the hydrolysis step, lower than 10% by weight.

The base is used in an aqueous solution at a concentration preferably ranging from 0.1 to 35% by weight. In particular, aqueous solutions of ammonia are used, preferably in a concentration ranging from 0.1 to 35% by weight.

The hydrolysis reaction is preferably carried out at a temperature ranging from 50 to 300°C and at a pressure ranging from 1 to 100 bar. The reaction can be carried out in an autoclave or in a reactor, operating in continuous. The autoclave or reactor are preferably made of stainless steel.

The glycerides present, mainly triglycerides, are hydrolyzed to the corresponding acids, with the formation of glycerine as by-product.

The mixtures deriving from the hydrolysis are subsequently treated so as to separate the fatty acids from the glycerine. Preferably the separation is of the physical type between the aqueous phase, in which the glycerine remains dissolved, and the phase formed by the fatty acids which, on the other hand, are insoluble in water. The fatty acids form the upper phase, whereas the aqueous phase containing the glycerine is the lower phase.

The small percentage of salts of acids with the base used which are possibly formed, is divided between the two phases.

The aqueous phase can also contain phosphoric acid if a mixture of a biological origin containing phosphoglycerides has been used.

Once the phases have been separated from the aqueous phase, using any technique known to skilled persons in the field, for example with a continuous Florentine separator, the glycerine is recovered by means of distillation. The remaining aqueous solution, possibly containing the base and possibly containing phosphoric acid, can be recycled to the hydrolysis step.

Before the hydrolysis step, the feedstock of a biological origin can be suitably treated so as to remove the content of alkaline metals (e.g. Na, K) and alkaline earth metals (e.g. Ca), possibly contained in the feedstock. This pre-treatment can be effected by adsorption on a suitable material: for example, the known percolation techniques can be used, on a column filled with acid earth or clays such as, for example, acid montmorillonites, bentonites, smectites, sepiolites. For this purpose, products available on the market can be used, such as, for example, Filtrol, Tonsil, Bentolites H and L, SAT-1.

Alternatively, ion-exchange resins can be conveniently used, or blandly acid washings effected, for example, by contact with sulfuric, nitric or hydrochloric acid, preferably at room temperature and atmospheric pressure.

The stream of free fatty acids, immediately downstream of the separation step following hydrolysis, is neutralized with ammonia.

In said step, the acids are then salified to the

corresponding ammonium salts and, at the end of the neutralization, the content of free acids is lower than 0.1% by weight with respect to the total weight of the salts.

A quantity of ammonia ranging from 1/1 to 2/1 moles per mole of fatty acid is used.

The neutralization is preferably carried out in the presence of one or more surfactants, preferably non-ionic. All non-ionic surfactants known to skilled persons in the field can be used in the present invention, organic silicon esters are preferably used. The use of surfactants is aimed at controlling the possible formation of foams.

The surfactant can be used in a quantity ranging from 0.0001% by weight to 2 % by weight with respect to the solution of ammonia.

The neutralization is preferably carried out at a temperature ranging from 50 to 300°C and a pressure ranging from 1 to 100 bar.

Gaseous ammonia or ammonia in aqueous solution can be used. The aqueous solutions of ammonia that can be used, preferably have a concentration ranging from 0.1 to 35.0% by weight, preferably 5-35%. The salification is effected in an autoclave or continuous reactor, made of stainless steel, particularly AISI 316, AISI 318 or AISI 321.

At the end of the neutralization step, the mixture of ammonium salts is separated from the ammonia and water, if present, by distillation of the ammonia solution. The ammonia solution thus separated can be subsequently treated with exchange resins to eliminate traces of ammonium salts remaining dissolved and can be

recycled to the neutralization step.

When the neutralization is carried out by means of gaseous ammonia, the excess ammonia is removed by means of stripping, i.e. by simple distillation with the removal of the most volatile component.

Alternatively, the mixture resulting from the neutralization, containing ammonium salts of fatty acids, ammonia and water, can be fed directly to the following hydroisomerization step.

If the salts have been isolated from the ammonia, before being fed to the HDO step, they can be slightly heated, to a temperature lower than 100°C, in order to make them liquid, or they can be dissolved in a solvent, selected for example from saturated hydrocarbons, in particular linear paraffins, for example n-hexane.

In the third step, the hydrodeoxygenation step (HDO), the mixture of ammonium salts of fatty acids is hydrodeoxygenated with hydrogen in the presence of a hydrodeoxygenation catalyst.

In this step, there is the hydrogenation of the double bonds present in the aliphatic chains of the salified fatty acids and deoxygenation by means of decarboxylation with the formation of carbon dioxide, carbon monoxide and ammonia.

Catalysts that can be used are all hydrogenation catalysts known in the art containing one or more metals selected from metals of group VIII and group VIB, suitably supported. Carriers suitable for the purpose are composed of one or more metal oxides, preferably alumina, silica, titania, zirconia or mixtures thereof. The metal(s) are preferably selected

from Pd, Pt, Ni, or from pairs of metals Ni-Mo, Ni-W, Co-Mo and Co-W, Ni-Mo and Co-Mo being preferred.

These catalysts are typically prepared by impregnation of the oxide carrier with a solution of a suitable salt of the metal or metals. The impregnation is then followed by thermal treatment in a suitable atmosphere for decomposing the precursor salt and obtaining the supported metal. Subsequent impregnations can be effected for both reaching the desired level of loading of the metal and also for differentiating, in the case of more than one metal, the supporting of the same. Processes are also known for the production of said catalysts, instead of by impregnation, by precipitation of the metal precursor from a saline solution of the metal itself on the carrier, or by co-precipitation of the various components of the catalyst, i.e. the metal and carrier.

Catalytic compositions such as Ni-Mo-P on zeolite, Pd/Zeolite, Pt/MSA, wherein MSA is a silico-alumina can also be conveniently used, having particular characteristics, described in EP340868, EP659478, EP812804, and also used as carrier for the catalytic compositions used in the subsequent hydroisomerization step. Catalysts which can be conveniently used in the HDO step of the present invention are described, for example, in J.T Richardson, "Principal of catalyst development", Plenum Press, New York, 1989, Charter 6.

Catalysts of the type Ni-Mo, Ni-W, Co-Mo and Co-W are preferably previously sulfidized. The pre-sulfidation procedures are effected according to the known techniques.

In order to keep the catalyst in sulfidized form,

the sulfidizing agent, for example, dimethyldisulfide, is fed contemporaneously to the feedstock of a biological origin, after a possible purification step of said feedstock, with a content ranging from 0.02 to 0.5% by weight (140-3400 ppm S).

Alternatively, the co-feeding of a "straight run" gasoil can be effected, with a high content of S(S >1%), at a concentration which is such as to approach the same overall content of S in the feedstock.

The HDO reaction is carried out in a reaction area comprising one or more catalytic beds, in one or more reactors. According to a preferred aspect, it is carried out in a typical fixed-bed hydrotreating reactor. The flow of hydrogen and feedstock containing ammonium salts of fatty acids can be sent in equicurrent or in countercurrent. The reactor can have adiabatic catalytic beds in a number higher than or equal to 2. As this is an exothermic reaction, with the production of heat, there will be a temperature rise in each catalytic bed. By feeding a stream of hydrogen and/or liquid feedstock between one catalytic bed and another, at a certain temperature, it is possible to obtain a constant or increasing temperature profile. This operating mode is normally indicated as "splitted feed".

As an alternative to a reactor with adiabatic layers, resort can be made to a tube-bundle reactor. The catalyst is suitably charged inside the tubes, whereas a diathermic liquid (dowtherm oil) is sent into the mantle side with the aim of removing the reaction heat.

For a better regulation of the thermal profile in

the reactor, whether it be with adiabatic layers or a tube-bundle, the reactor itself can be run with the recirculation of a part of the effluents, according to the typology known as recycling reactor. The function of the recycling is to dilute the fresh feedstock in the reactor thus limiting the thermal peaks due to the exothermicity of the reaction. The recycling ratio, i.e. the amount of recirculated fraction with respect to the fresh feedstock can vary from 0.5 to 5 w/w.

A further reactor configuration which can be used for this application is a slurry reactor in which the hydrodeoxygenation catalyst is suitably formed in microspheres and dispersed in the reaction environment. The gas-liquid-solid mixing in this case can be favoured by mechanical stirring or by forced recirculation of the reaction fluids.

The HDO step is preferably carried out at a pressure ranging from 25 to 70 bar, preferably from 30 to 50 bar, and at a temperature ranging from 240 to 450°C, preferably from 270 to 430°C. It is preferable to operate with an LHSV ranging from 0.5 to 2 $hours^{-1}$, even more preferably from 0.5 to 1 $hour^{-1}$. The ratio of H_2/mixture of fatty acid ammonium salts preferably ranges from 400 to 2,000 Nl/l.

The effluents of the HDO step comprise a mixture of paraffins, ammonia and possibly water; the water is that formed by the reaction and possibly that fed together with the fatty acid salts. The separation is effected by means of a separation step and a washing step. In this respect, the effluents of the HDO step can be sent to a high-pressure gas-liquid separator. A gaseous phase is recovered, essentially consisting of

hydrogen, ammonia, water, CO and CO_2. PH_3 and H_2S can also be possibly present in small quantities. After separation, the gaseous phase is cooled and the water is separated by condensation.

The remaining gaseous phase is purified to allow the recycling of the hydrogen to the reaction step (4) and ammonia to the neutralization step (3). For the purification and separation, conventional industrial methods for the abatement of H_2S can be used, such as, for example, washing with amines, for example methyl-ethyl-amine (MEA)or di-ethyl-amine (DEA).

CO and CO_2 can be removed by absorption in suitable absorbing solutions: the CO, for example, can be absorbed in solutions of copper ammonia complexes, whereas the CO_2 can be absorbed by aqueous solutions of alkaline carbonates.

Hydrogen and ammonia can be separated by means of membranes or ammonia absorbing washings, for example magnesium oxide, sodium hydroxide, sodium carbonate, potassium hydroxide or similar materials, can be used as ammonia absorbent.

The liquid phase separated in the high-pressure separator consists of a hydrocarbon fraction, essentially consisting of linear paraffins, with a number of carbon atoms ranging from 14 to 21, prevalently from 15 to 19. Depending on the operating conditions of the separator, the liquid fraction can contain small quantities of H_2O and oxygenated compounds, such as for example alcohols and carbonyl compounds. The residual S can be less than 10 ppm. The liquid fraction can then be washed with a gaseous hydrocarbon, for example CH_4, or nitrogen or hydrogen,

in a stripper, in order to further reduce the water content.

The resulting hydrocarbon mixture is fed to the subsequent hydroisomerization step. The hydroisomerization step is carried out in the presence of hydrogen and a catalytic composition: all known hydroisomerization catalysts can be used: catalysts containing zeolites and/or metals of group VIII can be used, for example, and/or a carrier selected, for example, from alumina or silica. The zeolite can be selected from SAPO-11, SAPO-41, ZSM-22, ZSM-23 or ferrierite, the metal of group VIII is preferably Pt, Pd or Ni. Catalysts which can be used are, for example, Pt/ZSM-22/Al_2O_3 and Pt/ZSM-23/Al_2O_3. According to a particularly preferred aspect, in accordance with what is described in WO 2008/058664 and in WO2008/113492, a catalyst composition is used which comprises:

a) a carrier of an acid nature comprising a completely amorphous micro-mesoporous silico-alumina having a SiO_2/Al_2O_3 molar ratio ranging from 30 to 500, a surface area greater than 500 m^2/g, a pore volume ranging from 0.3 to 1.3 ml/g, an average pore diameter lower than 40 Å,

b) a metal component comprising one or more metals of group VIII, possibly mixed with one or more metals of group VIB.

Completely amorphous micro-mesoporous silico-aluminas which can be used as carrier (a) of the catalytic compositions of the hydroisomerization step of the present invention are described in US 5049536, EP 659478, EP 812804, and called MSA. Their XRD powder spectrum does not have a crystalline structure and does

not show any peak. US 5049536, EP 659478, EP 812804 also describe various methods for preparing silico-aluminas suitable as carrier (a).

With respect to the metals contained in the metal component (b) of the catalytic compositions which can be used in the hydroisomerization step of the process of the present invention, this can be selected from metals of group VIII, possibly mixed with one or metals of group VIB. Compositions containing metals of group VIII alone are preferred. The metal or metals of group VIII are preferably selected from Pt, Pd, Ni and Co. In particular, when the metallic component contains only metals of group VIII, the metal or metals are preferably selected from Pt, Pd and Ni. When the metallic component contains both one or more metals of group VIII and one or more metals of group VIB, the metal of group VIII is preferably selected from Ni and Co. The metal of group VIB is preferably selected from Mo and W. The metal of group VIII is preferably in a quantity ranging from 0.1 to 5% by weight with respect to the total weight of the catalytic composition. The metal of group VIB, when present, is in a quantity ranging from 1 to 50, even more preferably in a quantity ranging from 5 to 35% by weight with respect to the total weight of the catalytic composition. The weight percentage of the metal, or metals, refers to the metal content expressed as a metallic element; in the final catalyst, after calcination, said metal is in the form of an oxide.

Catalytic compositions which can be conveniently used in the hydroisomerization step containing one or more metals of group VIII and additionally one or more

metals of group VIB, and their preparations, are described in EP 908231 and EP 1050571.

The hydroisomerization catalyst can be formulated and formed into extruded products having different forms (e.g. cylindrical, trilobal, etc.) as described, for example, in EP 1101813.

The type of reactor for the hydroisomerization step (6) is a fixed-bed reactor. The thermal control, in this case, is not critical as the reaction is slightly exothermic. For this purpose, a reactor with adiabatic layers is suitable. A tube-bundle reactor can in any case also be used.

The liquid feedstock deriving from the hydrodeoxygenation step can be sent into the reactor in equicurrent or in countercurrent with respect to the hydrogen.

The hydroisomerization can be carried out at a temperature ranging from 250 to 450°C, preferably from 280 to 380°C, and at a pressure ranging from 25 to 70 bar, preferably from 30 to 50 bar. It is preferable to operate with a LHSV ranging from 0.5 to 2 $hours^{-1}$. The H_2/HC ratio preferably ranges from 200 to 1,000 Nl/l.

The reaction conditions can be suitably selected for obtaining a product whose characteristics are balanced in relation to the cold properties of the diesel cut and gasoline cut with which the hydroisomerization product is subsequently mixed for preparing the hydrocarbon compositions of the present invention. The mixture resulting from the hydroisomerization step is subjected to distillation to obtain a purified hydrocarbon mixture which is used as fuel or as component of a biological origin in

hydrocarbon components which can be used as fuels.

Figure 1 shows an example of a scheme relating to the process of the present invention. The mixture of a biological origin is fed to the hydrolysis reactor (a) through line 1. The water, possibly containing a base, is fed to the hydrolysis reactor (a) through line 2. The mixture resulting from the hydrolysis, containing fatty acids, water, possibly a base, and possibly phosphoric acid is sent through line 3 to the separator (b). The phase containing fatty acids is separated, in said separator, from the aqueous phase containing glycerine, possibly a base and possibly phosphoric acid. The aqueous solution containing glycerine, possibly a base and possibly phosphoric acid is sent, through line 4, to the separation column (f) from which the glycerine is recovered, through line 14, and the water, possibly containing a base and possibly phosphoric acid, through line 13.

The fatty acids leaving the separator (b) are sent, through line 5, to the neutralization reactor (c), where they react with the ammonia, fed to the reactor (c) through line 6. The mixture leaving the neutralization reactor (c) is sent to the distillation column (d) to separate the fatty acid ammonium salts from the solution of water and ammonia, which is recovered through line 8. The fatty acid ammonium salts are sent to the hydrodeoxygenation (HDO) reactor (e) through line 9, whereas the hydrogen is fed to said reactor (e) through line 10. The mixture leaving the hydrodeoxygenation reactor (e) is sent to the high-pressure gas-liquid separator (h) through line 12. The gaseous phase comprising hydrogen, ammonia, water, CO

and CO_2, is recovered, through line 11, leaving the separator, and the liquid phase containing paraffins is recovered through line 15, which is sent to the hydroisomerization reactor (g). Hydrogen is fed to the hydroisomerization reactor through line 16. The mixture leaving the reactor (g), containing isomerized paraffins, is recovered through line 17.

CLAIMS

1) A process for the production of hydrocarbon mixtures starting from a mixture of a biological origin containing fatty acid esters with glycerine, and possibly containing free fatty acids and/or phosphoglycerides, which comprises:

- subjecting the mixture of a biological origin to hydrolysis, obtaining a mixture containing glycerine and containing a mixture of fatty acids,
- neutralizing the mixture of fatty acids with ammonia,
- subjecting the neutralized mixture to hydrodeoxygenation,
- subjecting the mixture resulting from the hydrodeoxygenation to hydroisomerization.

2) The process according to claim 1, comprising:

1) subjecting the mixture of a biological origin to hydrolysis, obtaining a mixture containing the corresponding fatty acids and glycerine,
2) separating the glycerine from the mixture of fatty acids,
3) neutralizing the mixture of fatty acids with ammonia, obtaining the corresponding ammonium salts,
4) subjecting the mixture of ammonium salts to hydrodeoxygenation obtaining ammonia and a mixture containing paraffins,
5) separating the ammonia from the mixture containing paraffins,
6) subjecting the mixture containing paraffins to hydroisomerization.

3) The process according to claim 1, wherein the mixture of a biological origin contains a quantity of fatty acids higher than 0 and lower than or equal to 60% by weight.

4) The process according to claim 1, wherein the mixtures of a biological origin are selected from vegetable oils, vegetable fats, animal fats, fish oils, algal oil or mixtures thereof.

5) The process according to claim 1, wherein the hydrolysis is carried out operating in the presence of water.

6) The process according to claim 5, wherein a base is present.

7) The process according to claim 6, wherein the base is selected from ammonia, aliphatic amines and ethanolamine.

8) The process according to claim 7, wherein the base is ammonia.

9) The process according to claim 6, wherein the base is used in a quantity ranging from 0.1/1 to 4/1 moles per mole of fatty acid ester.

10) The process according to claim 1, wherein the hydrolysis is carried out at a temperature ranging from 50 to 300°C and at a pressure ranging from 1 to 100 bar.

11) The process according to claim 5, wherein the glycerine is recovered by phase separation between the fatty acid phase and the aqueous phase, containing glycerine and possibly the base, followed by separation of the glycerine from the aqueous phase.

12) The process according to claim 1, wherein the neutralization of the fatty acids is effected with

ammonia.

13) The process according to claim 2 or 12, wherein the ammonia is in a quantity ranging from 1/1 to 2/1 moles per mole of fatty acid.

14) The process according to claim 1, wherein the neutralization is carried out in the presence of surfactants.

15) The process according to claim 1, wherein the neutralization is carried out at a temperature ranging from 50 to 300°C and a pressure ranging from 1 to 100 bar.

16) The process according to claim 1, wherein the hydrodeoxygenation is carried out in the presence of hydrogen and a hydrodeoxygenation catalyst.

17) The process according to claim 16, wherein the catalyst contains one or more metals selected from metals of group VIII and group VIB and a carrier.

18) The process according to claim 1, wherein the hydrodeoxygenation is carried out at a pressure ranging from 25 to 70 bar and a temperature ranging from 240 to 450°C.

19) The process according to claim 1 or 2, wherein ammonia and a mixture of paraffins are obtained from the hydrodeoxygenation, the ammonia is separated from the paraffins and recycled to the neutralization.

20) The process according to claim 1, wherein the hydroisomerization is carried out at a temperature ranging from 250 to 450°C and a pressure ranging from 25 to 70 bar.

21) The process according to claim 1, wherein the mixture of a biological origin contains phosphoglycerides and phosphoric acid is formed in the

hydrolysis step.

22) The process according to claim 21, wherein the phosphoric acid is separated together with the glycerine from the mixture of fatty acids.

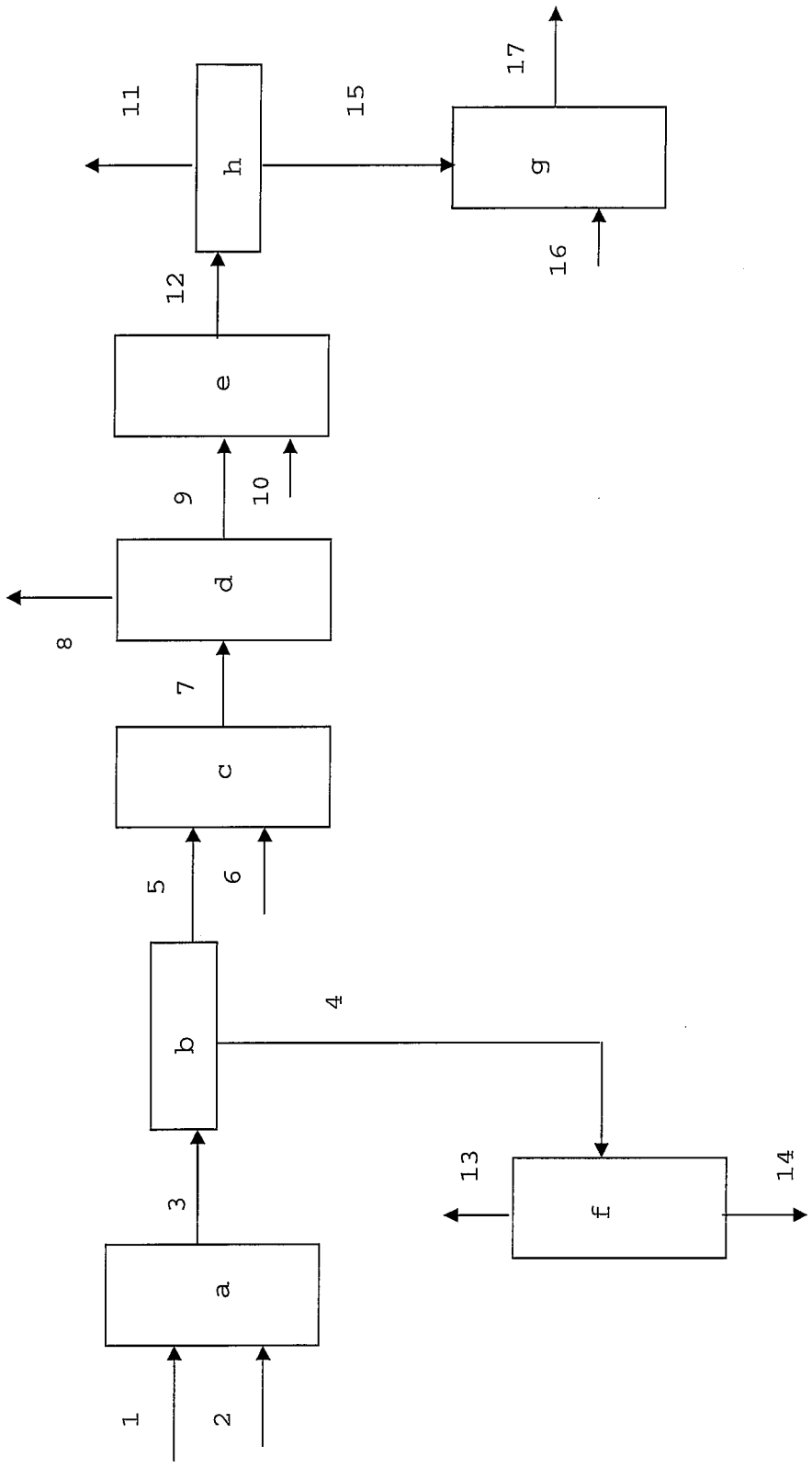

Fig.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/050336

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G45/58 C10G3/00 C07C1/20 C11B3/00 C11C3/12
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G C07C C11B C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013/310620 A1 (KALNES TOM N [US]) 21 November 2013 (2013-11-21) paragraphs [0001], [0010]; claims 1,15,17,27,29; figure 1	1-22
Y	EP 2 290 035 A1 (TOTAL PETROCHEMICALS RES FELUY [BE]) 2 March 2011 (2011-03-02) claims 1,4; figure 3	1-22
Y	US 8 440 875 B1 (EIZENGA DONALD A [US]) 14 May 2013 (2013-05-14) column 2, line 63 - column 3, line 53; claim 1; figure 1 column 4, line 55 - column 5, line 48 column 6, line 45 - line 59	1-22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"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	Date of mailing of the international search report
27 March 2015	08/04/2015

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2015/050336

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CN 102549112 A	04-07-2012
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US 8440875 B1	14-05-2013	NONE	