Title: A METHOD FOR THE PRODUCTION OF BIODIESEL, STARTING FROM HIGH IODINE NUMBER FATTY SUBSTANCES

Abstract: In its most general aspect, the present invention relates to the use of fatty substances having a iodine number greater than 135 gI2/100g, preferably greater than 140 gI2/100g, more preferably greater than 150 gI2/100g, for the production of biodiesel. In particular, the invention relates to a method for the production of biodiesel starting from fatty substances having a iodine number greater than 135 gI2/100g, preferably greater than 140 gI2/100g, more preferably greater than 150 gI2/100g, comprising the following steps: a) esterification of the fatty acids or transesterification of the triglycerides present in the aforementioned fatty substances with a C1-C10 alkyl alcohol, optionally in the presence of a suitable catalyst; b) the selective hydrogenation of the fatty acid alkyl esters obtained in step a) in the presence of a catalyst allowing the attainment of a biodiesel with a degree of unsaturation (evaluated as the iodine number) less than or equal to 120 gI2/1000 g and which is liquid at temperatures greater than or equal to -20°C. Between step a) and step b) there may also optionally be a step a) for the separation of the fatty acid alkyl esters obtained in step a) from the non-esterified resin acids.
DESCRIPTION

"A method for the production of biodiesel, starting from high iodine number fatty substances"

The present invention relates to the use of fatty substances with a iodine number greater than 135 gI₂/100g for the production of biodiesel, a method for producing biodiesel and the use of a catalyst for said production.

Biodiesel may be represented chemically as a mixture of fatty acid methyl esters. It is a naturally derived liquid fuel, produced from renewable sources which, in compliance with appropriate prescriptions, may be used in place of diesel fuel for both internal combustion engines and for producing heat in boilers.

The advantages, especially environmental, which can potentially result from the widespread use of biodiesel, are manifold:

- being a naturally derived material, and thus produced from photosynthesis, its combustion does not contribute towards increasing the net atmospheric carbon dioxide concentration, one of the major factors responsible for the greenhouse effect. For this reason, biodiesel is one of the fuels whose use should allow the objectives envisaged in the Kyoto agreement to be achieved;}
• considering the fact that the triglyceride oils used for the production of biodiesel are sulphur free, and that sulphur is not added to the end product in any way, the use of biodiesel does not contribute towards the phenomenon of acid rain;

• due to its particular composition, biodiesel is biodegradable and allows reduced emissions, in terms of particulates and polycyclic aromatic hydrocarbons. Instead, the results of the combustion of biodiesel are contentious in relation to so-called NOx emissions, where it has been observed that such emissions are more or less increased, with respect to conventional diesel, depending on the characteristics of the engine in which it is used;

• for economies like the European economy, which has to sustain the demand for energy with massive imports of fossil fuels, this is an excellent opportunity to have available an autonomous, as well as renewable energy source. The European Union strongly encourages this initiative, which allows the use of marginal land, not dedicated to food production, with undoubted advantages for safeguarding and increasing the work force and protecting and safeguarding the environment.

The production of this alternative fuel has seen
enormous developments over the past fifteen years, during which production has progressed from the trial stage to annual global production of 3,000,000 tons (2003 data), the majority of which of European origin.

Biodiesel is normally produced by starting from vegetable oils having a iodine number of less than or equal to 130, i.e. having a low unsaturation index, such as rape seed oil (IV=112), sunflower oil (IV=123), soybean oil (IV=130). Numerous production trials, also available in the literature, refer to the use of fatty substances of animal origin, as well as the use of recycled oils, such as those derived from frying, characteristic of the food industry.

In any case, and independently of the raw materials used, biodiesel marketed for consumption must comply with the various prescriptions made official through the European standards EN 14213:2003 and EN 14214:2003, which establish the minimum characteristics biodiesels must possess for use in boilers and haulage, respectively.

Finally, it should be remembered that, with standard biodiesel being obtained through the transesterification of a triglyceride oil with methyl alcohol, the production of fatty acid methyl esters (representing the major biodiesel product) is always
accompanied by the production of the by-product glycerol, in quantities equal to approx. 10 % by weight of the vegetable oil processed. This means that in 2003, approx. 300,000 tons of glycerol came onto the global market from biodiesel.

Despite all the economies of scale introduced, the production cost of biodiesel is not entirely competitive with that of regular diesel fuel of fossil origin, and its survival on the market depends on exemption from the payment of duties decided by the European Member states at the behest of the EU, which identify in biodiesel, one of the few products capable of complying with the prescriptions envisaged in the Kyoto agreement.

Thus, biodiesel would be a good alternative to diesel fuel of fossil origin, but its production still has a number of problems, including the following:

- the availability of raw materials at a stable price and compatible with the sale price of biodiesel, which, for commercial reasons, can never exceed that of diesel fuel of mineral origin;

- the requirement for sufficiently large quantities of fatty substances for energy purposes which has forced operators to purchase raw materials on the global market, and the increased demand has fatally lead to increased prices, even for the food sector;
the search for alternative raw materials, which cannot be used by the food industry, has consequently experienced a great upsurge, giving rise to embodiments based on the use of non-edible animal fats, residual oils from industrial frying, and industrial oil farming. The initiatives, which have certainly experienced some success, have however encountered certain problems that have not been easy to resolve, such as the poor cold resistance of biodiesel derived from animal fats, the difficulty in complying with the prescriptions relating to the maximum Conradson Carbon Residue content for recycled oils, caused by the presence of triglyceride polymers as a result of the heat-shock they have been subjected to, the poor stability to oxidation shown by highly unsaturated alternative oils, etc.. Furthermore, it should not be forgotten that the glycerol derived from the processing of such materials has an appearance and quality that are somewhat questionable, and is often not marketable, thus representing an economic burden, due to the costs associated with its disposal;

• the glycerol produced as a by-product of the biodiesel production technology (300,000 tons/year) represents 50 % of global consumption, and this has
contributed towards the collapse of the price of this polyalcohol, the problems associated with the marketing of which risk endangering the economic production of biodiesel.

Hence, there is a need to provide a method for the production of biodiesel which allows the above described drawbacks to be overcome.

In its most general aspect, the present invention relates to the use of fatty substances having a iodine number greater than 135 gI₂/100g, preferably greater than 140 gI₂/100g, more preferably greater than 150 gI₂/100g, for the production of biodiesel.

In particular, the invention relates to a method for the production of biodiesel, using fatty substances having a iodine number greater than 135 gI₂/100g, preferably greater than 140 gI₂/100g, more preferably greater than 150 gI₂/100g, as starting product.

The fatty substances preferably used for the purposes of the invention are tall oil and high degree of unsaturation vegetable and animal oils. The vegetable oils are selected from: linseed oil (IV=184), burdock oil (IV=153), hemp oil (IV=160), walnut oil (IV=145), poppy oil (IV=140), perilla seed oil (IV=204), camelina seed oil (IV=135), tung oil (IV=168) and mixtures thereof.
The animal oils are preferably fish oils. The fish oils are selected from shad oil (IV=175), cod liver oil (IV=160), herring oil (IV=140), salmon oil (IV=161), sardine oil (IV=185) and mixtures thereof.

Tall oil is a by-product of the paper industry, whenever this is prepared according to the KRAFT process. Said material consists of a mixture of highly unsaturated fatty acids (many of which with conjugated diene systems) and terpene derived resin acids, such as abietic acid (C_{20}H_{30}O_{2}) and pimaric acid (C_{20}H_{30}O_{2}). In crude tall oil, the resin acids are present in concentrations even exceeding 30 % m/m. Tall oil has a iodine number equal to approx. 170 gI₂/100 g.

Linseed oil has a high content of C18:3, fatty acids with a high degree of unsaturation. Indeed, the iodine number of linseed oil is around 170 gI₂/100 g.

The fish oil used for the purposes of the invention is preferably obtained from the processing of fish waste. Fish oil also has a iodine number equal to around 170 gI₂/100 g and is made up of polyenes such as C18:4, C20:4, C20:5, C22:5 and C22:6.

The fatty acids constituting the fatty substances having a iodine number greater than 135 gI₂/100g have an excessively high degree of unsaturation, making such substances unsuitable for the preparation of biodiesel
conforming to the reference standards. This fact, together with the conspicuous presence of conjugated diene systems, is the cause of the marked reactivity of the fatty acids of such substances which, when considered in relation to biodiesel, explain the very low or non-existent resistance to oxidation. On the contrary, resistance to oxidation is one of the main factors which qualify a biodiesel as being of good quality.

In the case of tall oil, the presence of resin acids results in increased Conradson Carbon Residue, that is to say the tendency for the fuel to form carbon deposits when used with stoichiometric quantities of comburent, such as for example in diesel cycle engines.

Past attempts to reduce the degree of unsaturation of the fatty acids in the highly unsaturated fatty substances, using hydrogenation, lead to derivatives that were unsuited to the manufacture of biodiesel. Indeed, partial hydrogenation of the highly unsaturated fatty substance fatty acids, performed using conventional catalysts, leads to the production of significant quantities of high melting point saturated fatty acids, which prejudice the cold-weather behaviour of the product obtained.

The major fatty acids present in the plant-derived
fatty substances of the invention are linolenic acid (9,12,15-octadecatrienoic, C18:3), linoleic acid (9,12-octadecadienoic, C18:2) and the conjugated isomers thereof and oleic acid (9-octadecenoic, C18:1).

Their rates of oxygen absorption are 800:100:1 respectively, hence partial hydrogenation with consequent lowering of the iodine number would lead to a significant increase in oxidative stability, particularly when C18:3 is reduced.

Analogous considerations are valid for the reduction of the polyunsaturated components (up to 6 double bonds) of fish oil.

The degree of unsaturation of the fatty acids is normally expressed as the iodine number, i.e. the number of grams of iodine that have reacted with 100 g of product analysed. The higher the index (number), the greater the degree of unsaturation. For example, for biodiesel intended for haulage use, the most remunerative use, a maximum iodine number limit is envisaged of 120 gI₂/100g, while, as already mentioned, the fatty substances of the invention have a iodine number greater than 135 gI₂/100g.

On the other hand, in order to preserve the fluidity of the oil, it is essential not to increase the melting point, which depends on the content of the
saturated component (stearic acid C18:0) and the quantity of trans and positional isomers, the formation of which is inevitable during the hydrogenation process.

Indeed, in that respect, it should be noted that both the oleic acid isomers where the double bond is in a position other than the natural position, i.e. 9(10), and the trans isomer of oleic acid (elaidic), have melting points that are much higher than natural oleic acid, and their presence might significantly compromise the cold-weather properties, very important for diesel fuels, as highlighted in the following table:

**Table 1: The influence of double bonds number, position and geometry on the melting points of the 18 carbon atom fatty acids**

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>N° of double bonds</th>
<th>MP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9,12,15 C18:3</td>
<td>3</td>
<td>-13</td>
</tr>
<tr>
<td>9,12 C18:2</td>
<td>2</td>
<td>-7</td>
</tr>
<tr>
<td>9 C18:1</td>
<td>1</td>
<td>+16</td>
</tr>
<tr>
<td>C18:0</td>
<td>0</td>
<td>+70</td>
</tr>
</tbody>
</table>

Monounsaturated fatty acid: influence of double bond position

<p>| Δ6                  | 28                  | 53      |</p>
<table>
<thead>
<tr>
<th>Δ⁹</th>
<th>16</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ¹²</td>
<td>27</td>
<td>52</td>
</tr>
<tr>
<td>Δ¹⁵</td>
<td>40</td>
<td>58</td>
</tr>
</tbody>
</table>

Thus, in order to use fatty substances having iodine numbers greater than 135 gI₂/100g, preferably greater than 140 gI₂/100g, more preferably greater than 150 gI₂/100g, for the production of biodiesel, it is essential to have a hydrogenation catalyst which reduces the degree of unsaturation by as much as possible, without however increasing the stearic acid content and limiting cis-trans and positional isomerisation by as much as possible. Furthermore, in the case of tall oil, it is essential to reduce the resin acid content, which results in increased Conradson Carbon Residue with consequences for the good operation of the fuel, by as much as possible.

The scientific and patent literature relating to hydrogenation catalysts is extremely poor, since that degree of selectivity is difficult to achieve with the Ni and noble metal-based catalysts normally used industrially. In particular, the hydrogenation of fatty substances with high degrees of unsaturation has been rarely studied, and never with the aim of producing good quality biodiesel.
The patent application RU 2174973 C1 reports the hydrogenation of tall oil, over a supported Ni catalyst, to oleic acid with a yield > 85% but does not specify either the distribution of the cis, trans and positional isomers, nor the physical properties of the oil thus obtained. Furthermore, in all the examples reported, a consistent increase in stearic acid is obtained.

The hydrogenation of other oils, again over a Ni catalyst, leads to products with high oleic acid 79% or stearic acid 80% contents, depending on the experimental conditions. Such oils may be used as plasticisers and vulcanisation activators (Kauchuk i Rezina, 1996, in Russian, CAN 126:331500).

The fatty substances of the invention, besides a high linoleic acid (C18:2) content, also have a significant amount of conjugated diunsaturated acids (C18:2 con), which are much more reactive, with respect to hydrogenation.

As a result of the increased reactivity and the altered absorption of such conjugated acids onto the surface of the catalyst, the selection of a catalyst which allows selective hydrogenation represents a problem that is not easily solved.

However, the applicant has surprisingly found that using catalysts consisting of copper on suitable solid
supports, for the hydrogenation of high iodine number fatty substances, good selectivity and activity are obtained.

Hence, in one aspect, the present invention relates to a method for the production of biodiesel consisting of the following steps:

a) esterification of the fatty acids or transesterification of the triglycerides of fatty substances having a iodine number greater than 135 gI₂/100g, preferably greater than 140 gI₂/100g, more preferably greater than 150 gI₂/100g, with a C₁-C₁₀ alkyl alcohol, optionally in the presence of a suitable catalyst;

b) selective hydrogenation of the fatty acid alkyl esters obtained in step a) in the presence of a catalyst, allowing the attainment of a biodiesel with a degree of unsaturation less than or equal to 120 gI₂/100 g and which is liquid at temperatures greater than or equal to -20°C.

In the case where tall oil is used as the starting vegetable oil in the above described process, then an additional step a1) is introduced between steps a) and b), involving the separation of the fatty acid alkyl esters obtained in step a) from the non-esterified resin acids.
In step a), the preferred starting product for the method of the present invention is tall oil, vegetable or animal oils, preferably fish oils. Whenever tall oil is used, this preferably has a resin acid content ranging between 1 and 25% m/m, preferably between 1 and 15% m/m, and more preferably between 2 and 7% m/m. Furthermore, tall oil may optionally be distilled prior to use in the method of the invention, so as to reduce the resin acid content. In this case, reference is made to "tall oil fatty acids". Tall oil colophony (rosin), a mixture of resin acids with varying degrees of purity, which finds a number of uses in those industries using natural resins for the production of lacquers, paints, hydrophobic coatings, inks, loads for plastics etc., is obtained as a by-product of said distillation.

The alkyl alcohol used for the esterification or transesterification in step a), preferably has from 1 to 10 carbon atoms, more preferably from 1 to 5 carbon atoms and even more preferably, is methyl alcohol.

In the case of vegetable or plant oils which are triglycerides, step a) is a transesterification step, carried out according to the procedures of the known art.

In the case of tall oil, consisting of fatty acids, step a) is an esterification step, preferably carried
out in the presence of a homogeneous or heterogeneous catalyst. The homogeneous catalyst is an acid compound, for example concentrated sulphuric acid, p-toluenesulphonic acid monohydrate, gaseous hydrochloric acid, phosphoric acid or methanesulphonic acid.

The heterogeneous catalyst is advantageously a metallic oxide selected from: ZnO, SnO, CaO.

A homogeneous catalyst is preferably used for the esterification reaction of step a).

Typically, in step a), the high degree of unsaturation fatty acids are mixed with an excess of the alkyl alcohol and the catalyst, and the reaction is initially carried out at the boiling point of the alkyl alcohol used. Due to the formation of water, the temperature increases over the course of the reaction. Upon completion of the reaction, if an acid catalyst has been used, the mixture is neutralised through the addition of a suitable base, for example NaOH. This leads to the formation of a salt, which precipitates from the mixture and must be separated out, for example by means of filtration. If a heterogeneous catalyst is used, then upon completion of the reaction, the solid catalyst is separated from the reaction mixture, for example by means of filtration, and all the operations necessary for the recycling of the catalyst are
performed, for example washing and drying.

The excess alkyl alcohol and water mixture is separated from the mixture containing the reaction product (i.e. the high degree of unsaturation fatty acid alkyl esters) and the unreacted resin acids, in the case of tall oil, by means of evaporation under vacuum. The water is then removed from the alkyl alcohol by means of distillation, and the alkyl alcohol recovered and recycled.

Alternatively, the reaction of step a) may be carried out at temperatures greater than the boiling point of the alkyl alcohol, for example at approx. 150°C, thus increasing the pressure appropriately. This solution is preferred whenever a heterogeneous catalyst is used. Or, the reaction may be carried out in two or more steps with the intermediate elimination of the water and alkyl alcohol, and the regeneration of the alcohol alone.

Where tall oil is used, during the esterification reaction, the resin acids present in the starting product are not esterified and may be separated and recovered in step a1) thanks to the differences in volatility.

The separation of the fatty acid alkyl esters obtained in step a) from the non-esterified resin acids
is advantageously carried out by means of distillation under vacuum using suitable discontinuous distillation equipment, or in continuous stills, for example thin film stills. The preferred distillation temperature is between 140 and 220°C, preferably between 180 and 200°C. The residual pressure is between 1 and 10 mbar, preferably between 1 and 5 mbar.

Distillation is preferably performed after having heated the starting product to a temperature of approx. 100°C under vacuum, for the amount of time required for its complete degassing and anhydration.

This operation accomplishes two main objectives:

i) the forced removal of the resin acids, thus allowing the use of only partially refined tall oil, and hence the use of low cost raw materials;

ii) a potential reduction in the Conradson Carbon Residue;

iii) a thorough cleaning of the substrate prior to moving onto the selective hydrogenation of step b), thus allowing the standardisation of the experimental hydrogenation conditions, as well as reduced amounts of hydrogenation catalyst which, by being able to operate in a clean environment and with reduced concentrations of agents inhibiting its activity, may easily be reused in the case of batch reactions, or with its operational
lifespan foreseeably being increased in the case of continuous embodiments. Step a1), involving the distillation of the resin acids, is not performed when other fatty substances, such as for example vegetable oils and fish oil, not containing such resin acids, are used as the starting products.

The process thus proceeds directly to the selective hydrogenation of the fatty acid alkyl esters produced in step a), which leads to the forced removal of the conjugated polyene, triene or diene systems, the reduction of the linoleic acid alkyl ester content and thus an overall reduction of the iodine number, to numbers of less than the 120 gI₂/100g limit, and may further be adjusted and targeted, depending on the qualitative characteristics of the desired final product.

Selective hydrogenation is performed in the presence of a copper catalyst supported on a suitable solid support. Preferably, the catalyst is copper supported on Al₂O₃, SiO₂, sepiolite and TiO₂. Preferably, the catalyst of the invention is copper supported on Al₂O₃, sepiolite and TiO₂. Even more preferably, it is Cu/Al₂O₃.

Particularly, selective hydrogenation is carried out in any of the reactors known in the art, into which
the catalyst and the fatty acid alkyl ester mixture produced in step a) or a1) are introduced. The mixture is kept stirring and under a positive pressure of hydrogen of from 2 to 8 atm, preferably around 6 atmospheres. It is heated to a temperature of between 150 to 200°C, preferably around 180°C. The reaction times range between 30 minutes and 4 hours, preferably between 1 and 3 hours. Upon completion of the reaction, the catalyst is preferably washed, dried and recycled.

However, in another aspect, the present invention relates to the use of a copper catalyst supported on a suitable solid support for the selective hydrogenation of the fatty acid alkyl esters of fatty substances having iodine numbers greater than 135 gI₂/100g, preferably greater than 140 gI₂/100g, more preferably greater than 150 gI₂/100g.

By the selective hydrogenation of the fatty acid alkyl esters of such fatty substances is meant that the catalyst used in the present invention allows the removal of the conjugated and isolated polyenes and dienes with the formation of monoenes, without in any way achieving the complete saturation of the molecule, with the consequent formation of saturated fatty acids.

Preferably, the catalyst of the present invention is copper supported on Al₂O₃, SiO₂, sepiolite and TiO₂.
More preferably, the catalyst of the invention is copper supported on Al₂O₃, sepiolite and TiO₂. Even more preferably, it is Cu/Al₂O₃.

The silica used in the present invention is preferably mesoporous silica having a specific surface area ranging between 200 m²/g and 650 m²/g, preferably between 300 and 600 m²/g.

Said silica has a pore volume (PV) ranging between 0 and 2 ml/g, preferably between 0.8 and 1.2 ml/g.

The alumina used in the present invention preferably has a specific surface area ranging between 100 m²/g and 500 m²/g, preferably between 200 and 350 m²/g. Said silica has a pore volume (PV) ranging between 0.5 and 2 ml/g, preferably between 1 and 2 ml/g.

The sepiolite used in the present invention has a surface area of approx. 240 m²/g and PV of approx. 0.4 ml/g; with regard to the titanium used, this is a pyrogenic, and hence non-porous material, having a surface area of approx. 25 m²/g.

The catalyst of the invention is prepared by treating an aqueous solution of Cu²⁺ ions with a fine base, so as to obtain a clear solution. The solid support is then added, and the mixture kept stirring for from 15 minutes to 2 hours, preferably for approx. 20 minutes.
The solution is diluted so as to cause the deposition of the hydrogenolysis product onto the support, and the solid is separated from the solution by means of filtration, then dried and calcined in air.

Drying occurs at a temperature of between 110 and 150°C, preferably around 120°C, for a length of time ranging between 6 and 24 hours, preferably for approx. 12 hours. Calcination is carried out at a temperature ranging between 300 and 400°C, preferably at approx. 350°C, for a period of time ranging between 1 and 10 hours, preferably for approx. 3 hours. Prior to the selective hydrogenation of the fatty acid alkyl esters, the precursor of the catalyst thus obtained must be activated by air drying at a temperature ranging between 200 and 300°C, preferably around 270°C, for a period of time ranging between 15 minutes and 2 hours, preferably for approx. 20 minutes.

The reactor is subsequently closed and evacuated at the same temperature and for the same length of time. At the same temperature, H₂ is then introduced, and then all the water formed removed under vacuum. In order to be certain of having reduced all the metal oxide present, it is preferable to repeat the vacuum/H₂ cycle a second time.

ADVANTAGES
High iodine number fatty substances appear to be rather interesting raw materials for the production of biodiesel, due to their market availability (for example, tall oil is an unintentional by-product of paper production, fish oil is a by-product from the fish processing industry), due to their competitive price and, in relation to tall oil, due to the fact that, being constituted by free fatty acids and not triglycerides, it releases water instead of glycerol as a by-product of the esterification reaction, according to the reaction reported below:

$$R{-}\text{COOH} + \text{Alk-OH} \rightarrow R{-}\text{COOAlk} + \text{H}_2\text{O}$$

Fatty Acid Alkyl alcohol Alkyl ester Water

However, their use to date has been limited by the lack of an effective method of production and, particularly, an effective fatty acid hydrogenation method.

Thus, the present invention allows the use of high iodine number fatty substances as starting materials for the production of biodiesel, with the consequent advantages of using raw materials that are widely available and cheap, hence, providing a low cost fuel, the production cost of which is not influenced by problems associated with the marketing and/or disposal
of glycerine, when the raw material used is tall oil. Furthermore, the biodiesel production process according to the invention allows the recycling of the reagents and by-products, such as the alkyl alcohol, the catalysts and the water, all to the benefit of the environment.

The catalyst used in the present invention allows the removal of polyenes with the formation of monoenes, without in any way achieving the complete saturation of the molecule, with the formation of saturated fatty acid esters.

Consequently, the hydrogenation process of the diunsaturated 18 carbon atom fatty acid alkyl esters only gives rise to monoenes in the cis or trans configuration. Further confirmation of the specific and selective hydrogenation method is illustrated by the example deriving from monitoring the concentrations of palmitic and palmitoleic acids (C16, saturated and monounsaturated respectively), the concentrations of which remain constant over the course of the reaction, in as much as in the mixture, there are no 16 carbon atom fatty acid methyl esters with more than one double bond. A positive side effect of this treatment, in relation to the use of tall oil, is a further reduction in the Conradson Carbon Residue, which can be explained
by a reduction in diene systems (particularly conjugated systems) and thus the tendency of the mixture to polymerise, allowing the vaporisation and combustion of the molecules before said thermal polymerisation can occur.

EXPERIMENTAL SECTION

Preparation 1

The catalyst precursor

A solution of Cu(NO₃)₂·3H₂O in water has been treated with a slight excess of conc. NH₄OH until a clear solution is obtained. The support has been added to this solution and the mixture has been kept stirring for 20 minutes.

Finally, the mixture has been diluted so as to cause the decomposition of the finely dispersed hydrogenolysis product onto the support. The material has been separated by filtration, dried for 12 hours at 120°C and calcined in air for 3 hours at 350°C.

The following catalysts, containing approx. 8% Cu by weight on numerous supports, are thus obtained:

Precursor A

Silica gel support from Grace Davison, labelled SP 550-10018 with a specific surface area of 600 m²/g, PV = 0.99 ml/g.

Precursor B
Support: Al₂O₃ from Grace Davison, characterised by the label Davicat® SMR 24-847, with a specific surface area of 280 m²/g, PV = 1.75 ml/g.

Synthesis of the catalyst

Prior to the reaction, the precursor has been activated by air drying at 270°C for 20 minutes. The reactor has been subsequently closed and evacuated at the same T (temperature) for a further 20 minutes, then H₂ (1 atm) has been introduced, and still at 270°C, all the water formed has been removed under vacuum. In order to be certain of having reduced all the CuO present, it is preferable to repeat the vacuum/H₂ cycle a second time.

Catalysts A' and B' have thus been prepared starting from precursors A and B.

Synthesis of the biodiesel

Direct esterification of the tall oil fatty acids (step a))

100 parts by weight of tall oil fatty acids (6.7 % m/m resin acids) are reacted with 100 parts by weight of methyl alcohol, in the presence of 0.5 g (approx. 0.3 ml) of concentrated sulphuric acid or 1 g of para-toluenesulphonic acid monohydrate.

The reaction is carried out in a reactor fitted with a stirrer, a temperature monitoring and control
device, a reflux condenser and an access way for withdrawing samples.

The reaction is normally carried out at the mixture's boiling point, which initially coincides with that of pure methyl alcohol (64 °C), then being increased in parallel with the degree of progress of the reaction, due to the water formation. Said temperature increase is more sensitive the more the stoichiometric excess used is reduced.

The progress of the reaction is followed by means of periodic sampling and the determination of the residual acidity.

In order to calculate the real degree of advancement, it is necessary to subtract the catalytic agent's contribution towards acidity from the result obtained from the analysis, performed in accordance with ISO 660:1999.

An example is reported in table 2, which is intended to illustrate an example of the kinetics of the reaction carried out with toluenesulphonic acid catalysis.

Table 2

<table>
<thead>
<tr>
<th>Time, hours</th>
<th>Total acidity (mg KOH/g)</th>
<th>Contribution from the catalyst</th>
<th>Net acidity (mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

26
<table>
<thead>
<tr>
<th></th>
<th></th>
<th>(mg KOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.6</td>
<td>6.1</td>
</tr>
<tr>
<td>1</td>
<td>10.0</td>
<td>6.1</td>
</tr>
<tr>
<td>2.5</td>
<td>7.4</td>
<td>6.1</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Upon completion of the reaction, the residual acidity is neutralised through the addition of an aqueous solution of NaOH, and the excess methyl alcohol used, which is evaporated along with the water produced during the esterification reaction, recovered. The hydroalcoholic mixture is then sent to be separated by distillation, for the purification of the methyl alcohol to be recycled in the system, and the isolation and elimination of the reaction water.

Prior to performing the distillation step under vacuum, the mixture of methyl esters is subjected to filtration in order to eliminate any insoluble sodium sulphate (sodium para-toluene sulphonate) deriving from the neutralisation of the catalyst.

Additional possibilities: the use of alternative catalysts, conducting the reaction at high temperature and pressure, the use of heterogeneous catalysts, conducting the reaction in two or more steps, with the intermediate elimination of water and methyl alcohol and regeneration of the alcohol alone.
Distillation of the tall oil fatty acid methyl esters (step a1)

The mixture of tall oil fatty acid methyl esters as described in example A (above), still containing its original content of resin acids (which do not react in the methylation reaction under the experimental conditions adopted) is transferred into the high vacuum distillation apparatus fitted with a multi-necked round-bottomed flask with connections for monitoring the temperature, residual pressure, the mechanical stirring system, Claisen type vapour spray retention manifold, Liebig type indirect heat exchange condenser system, distillate collection device and high vacuum pump, of suitable capacity.

The simple distillation operation, conducted after having maintained the product at a temperature of approx. 100 °C under vacuum, for the entire time necessary for its degassing and anhydration, is typically performed at a temperature of 180-200 °C and at a residual pressure of 1-2 mbar (0.1 KPa).

The yield of the process depends on the resin acid content of the starting product. In a typical trial, the distillation operation allowed the reduction of the resin acid content of the methylated sample from 6.7 % (m/m) to 0.67 % of the sample prepared for distillation.
Example 1

Hydrogenation of tall oil methyl esters with catalyst A (step b))

Into the reactor, in which catalyst A (1.2 g) has just been prepared, have been loaded 60 ml of tall oil methyl esters having the composition indicated in the table by the reference initials SM.

The remaining 12.6% by weight not indicated in the table was constituted by palmitic, palmitoleic and erucic acids, which remain unaltered during the hydrogenation.

The reactor has been pressurised with H₂ (6 atm) the temperature adjusted to 180°C and the reaction mass subjected to stirring. Samples are withdrawn at 20 minute intervals, and analysed. When the analysis seems to satisfy the requirements (80 min.) the reactor is cooled and the mixture analysed to give the iodine number, the flow point, the Conradson carbon residue (0.01 %) and the Cu content (not detectable). The results are reported in Table 3.

Example 2

Hydrogenation of tall oil methyl esters with catalyst B (step b))

This is performed as in example 1 except that catalyst B has been used, and the reaction has been
interrupted after 80 minutes. The results are reported in table 3.

Example 3

Hydrogenation of tall oil methyl esters with catalyst B (step b))

This is performed as in example 1 except that 0.6 g of catalyst C have been used, and the reaction has been interrupted after 120 minutes. The results are reported in table 3.

Table 3

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Example 4

Hydrogenation of linseed oil methyl esters with
catalyst B (step b)), obtained by means of transesterification according to the known art.

This is performed as in example 1 except that 0.6 g of catalyst B have been used, and the reaction has been interrupted after 600 minutes. The results are reported in table 4.

Example 5

Hydrogenation of linseed oil methyl esters with catalyst A, obtained by means of transesterification according to the known art.

This is performed as in example 1 except that 0.6 g of catalyst A have been used, and the reaction has been interrupted after 800 minutes. The results are reported in table 4.

Example 6

Hydrogenation of fish oil ethyl esters with catalyst B, obtained by means of transesterification according to the known art.

This is performed as in example 1 except that 0.6 g of catalyst B have been used, and the reaction has been interrupted after 80 minutes. The results are reported in table 4.
### Table 4

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<th>C18:0</th>
<th>IV Iodine number (gI₂/100 g)</th>
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SM2 = linseed oil methyl esters
SM3 = fish oil ethyl esters

5
CLAIMS

1. A method for the production of biodiesel comprising the following steps:

   a) Esterification of the fatty acids of fatty substances having iodine numbers greater than 135 gI₂/100g, with a C₁-C₁₀ alky alcohol, optionally in the presence of a suitable catalyst;

   b) Selective catalytic hydrogenation of the fatty acid alkyl esters obtained in step a), with a degree of unsaturation of less than or equal to 120 gI₂/100 g and which are liquid at temperatures greater than or equal to -20°C.

2. The method according to claim 1 wherein said fatty substances have a iodine number greater than 140 gI₂/100g, preferably greater than 150 gI₂/100g.

3. The method according to claims 1 or 2 wherein step b) is conducted in the presence of a copper catalyst supported on Al₂O₃, SiO₂, sepiolite or TiO₂.

4. The method according to any claim 1 to 3 wherein step b) is conducted in the presence of a copper catalyst supported on Al₂O₃, sepiolite or TiO₂.

5. The method according to any claim 1 to 4 wherein step b) is conducted in the presence of a copper catalyst
supported on Al₂O₃.

6. The method according to any claim 3 to 5 wherein said SiO₂ is mesoporous silica having a specific surface area ranging between 200 m²/g and 650 m²/g, preferably between 300 and 600 m²/g.

7. The method according to any claim 3 to 5 wherein said silica has a pore volume (PV) ranging between 0 ad 2 ml/g, preferably between 0.8 and 1.2 ml/g.

8. The method according to any claim 3 to 6 wherein said alumina has a specific surface area ranging between 100 m²/g and 500 m²/g, preferably between 200 and 350 m²/g.

9. The method according to any claim 3 to 7 wherein said alumina has a pore volume (PV) ranging between 0.5 ad 2 ml/g, preferably between 1 and 2 ml/g.

10. The method according to any claim 3 to 8 wherein said sepiolite has a surface area of approx. 240 m²/g.

11. The method according to any claim 3 to 9 wherein said sepiolite has a pore volume of approx. 0.4 ml/g.

12. The method according to any claim 3 to 10 wherein said TiO₂ has a surface area of approx. 25 m²/g.

13. The method according to any claim 1 to 12 wherein step b) is conducted under a hydrogen pressure ranging between 2 and 8 atm, preferably around 6 atm.

14. The method according to any claim 1 to 13 wherein
step b) is conducted at a temperature ranging between 150 and 200°C, preferably at around 180°C.

15. The method according to any claim 1 to 14 wherein the reaction is carried out for a period of time ranging between 30 minutes and 4 hours, preferably between 1 hour and 3 hours.

16. The method according to any claim 1 to 15 wherein the catalyst of step b) is recycled upon completion of the reaction.

17. The method according to any claim 1 to 16 wherein said alkyl alcohol has from 1 to 10 carbon atoms, more preferably from 1 to 5 atoms

18. The method according to any claim 1 to 17 wherein said alkyl alcohol is methyl alcohol.

19. The method according to any claim 1 to 18 wherein step a) is conducted in the presence of a homogeneous or heterogeneous catalyst.

20. The method according to claim 19 wherein the homogeneous catalyst is an acid compound.

21. The method according to claim 20 wherein said homogeneous catalyst is selected from: concentrated sulphuric acid, p-toluenesulphonic acid monohydrate, gaseous hydrochloric acid, phosphoric acid or methanesulphonic acid.

22. The method according to any claim 19 to 21 wherein
said heterogeneous catalyst is a metal oxide selected from: Zn oxide, Sn oxide or Ca oxide.

23. The method according to any claim 1 to 22 wherein said alkyl alcohol is used in excess.

24. The method according to any claim 1 to 23 wherein step a) takes place at the boiling temperature of the alkyl alcohol.

25. The method according to any claim 1 to 24 wherein step a), in the case where a heterogeneous catalyst is used, is carried out at approx. 150°C, thus increasing the pressure appropriately.

26. The method according to any claim 19 to 25 wherein said heterogeneous catalyst is recycled upon completion of the reaction.

27. The method according to any claim 1 to 26 wherein in step a), the excess alkyl alcohol is recycled upon completion of the reaction.

28. The method according to any claim 1 to 27 wherein said fatty substances are selected from tall oil, vegetable or animal oils.

29. The method according to claim 28 wherein said vegetable oils are selected from the group constituted by linseed oil, burdock oil, hemp oil, walnut oil, poppy oil, perilla seed oil, camelina seed oil, tung oil and mixtures thereof.
30. The animal oils are fish oils selected from shad oil, cod liver oil, herring oil, salmon oil, sardine oil and mixtures thereof.

31. The method according to any claim 28 to 30 wherein, when said fatty substances are vegetable or animal oils, step a) is a triglyceride transesterification reaction.

32. The method according to any claim 28 to 31 wherein said tall oil has a resin acid content ranging between 1 and 15% m/m, preferably between 2 and 7% m/m.

33. The method according to any claim 1 to 32 including, between step a) and step b), in cases where tall oil is used as the starting product, a separation step a1) of the fatty acid alkyl esters obtained in step a) from the non-esterified resin acids.

34. The method according to claim 33 wherein said separation occurs by means of distillation under vacuum in suitable discontinuous distillation apparatus or in continuous stills.

35. The method according to claim 32 wherein said continuous stills are thin film stills.

36. The method according to any claim 33 to 35 wherein the distillation temperature ranges between 140 and
220°C, preferably between 180 and 200°C.

37. The method according to any claim 33 to 36 wherein distillation is conducted at a residual pressure ranging between 1 and 10 mbar, preferably between 1 and 5 mbar.

38. The method according to any claim 33 to 37 wherein distillation is performed after having heated the starting product to a temperature of approx. 100°C under vacuum, for the amount of time required for its complete degassing and anhydride.

39. The use of a copper catalyst supported on Al₂O₃, SiO₂, sepiolite or TiO₂ for the selective hydrogenation of Tall oil fatty acid alkyl esters.

40. The use according to claim 39 wherein said catalyst is copper supported on Al₂O₃, sepiolite or TiO₂.

41. The use according to claims 39 or 40 wherein said catalyst is Cu/Al₂O₃.

42. The use of fatty substances having a iodine number greater than 135 gI₂/100g, preferably greater than 140 gI₂/100g, more preferably greater than 150 gI₂/100g, for the production of biodiesel.
A. CLASSIFICATION OF SUBJECT MATTER
INV. C11C3/12 C16G3/00 C07C67/56 B01J23/50

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)
C11C C16G C07C B01J

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 practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:
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- "*E" earlier document but published on or after the international filing date
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- "*S" document member of the same patent family

Date of the actual completion of the international search
21 August 2006

Date of mailing of the international search report
29/08/2006

Authorized officer
Cagnoli, M
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