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(71) Applicants:

- **Petróleo Brasileiro S.A. - PETROBRAS
28999-999 Rio de Janeiro (BR)**
- **Universidade Federal Do Rio De Janeiro - UFRJ
21941-901 Rio De Janeiro - RJ (BR)**

(72) Inventors:

- **da Silva, Jose
22621-252 Rio de Janeiro (BR)**
- **Freire, Denise
22620-360 Rio de Janeiro (BR)**
- **Habert, Alberto
2261-310 Rio de Janeiro (BR)**
- **Soares, Valeria
22630-010 Rio de Janeiro (BR)**

(74) Representative: **Benson, John Everett**

**J A Kemp
14 South Square
Gray's Inn
London WC1R 5JJ (GB)**

(54) **Process for the production of bio-lubricant from methyl biodiesel and bio-lubricant obtained by said process**

(57) This invention describes a process for the production of bio-lubricant from castor oil methyl biodiesel (methyl ricinoleate) and/or from Jatropha oil methyl biodiesel (mixture of methyl oleate and linoleate) and its respective products.

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Description**FIELD OF THE INVENTION**

[0001] The present invention describes a process for the production of bio-lubricant from castor oil methyl biodiesel (methyl ricinoleate) and/or from Jatropha oil methyl biodiesel (mixture of methyl oleate and linoleate) as well as the following products: basic oil, methylolpropane trioleate and methylolpropane triricinoleate obtained by the respective processes.

PRIOR ART

[0002] Castor or ricin is the seed of *Ricinus communis* L., a species of the Euphorbiaceae family. The main product derived from this plant is castor bean oil, or castor oil.

[0003] Brazil is the third largest grower and producer of castor beans, behind only India and China. The composition of castor bean oil or castor oil is approximately 90% ricinoleic acid, which differentiates it from all other vegetable oils.

[0004] Ricinoleic acid (Figure 1A) is a fatty acid comprising 18 carbon atoms with a double bond between carbon 9 and 10 and a hydroxyl in carbon 12 of its chain.

[0005] There is no other vegetable oil produced commercially with this characteristic. This structural characteristic gives said oil a high viscosity and solubility in alcohol at temperatures ranging from 0°C to 30°C.

[0006] It is from castor oil that the raw material known as methyl biodiesel is obtained.

[0007] Jatropha comprises an oilseed rich in oleic and linoleic acids, from which biodiesel can be produced. Oleic acid (Figure 1 B) is also a fatty acid comprising 18 carbon atoms having a double bond in carbon 9. However, it does not have a hydroxyl in carbon 12.

[0008] Linoleic acid is an unsaturated fatty acid with 18 carbons having two unsaturates.

[0009] Together with the castor bean, Jatropha has great potential as a raw material for the synthesis of bio-lubricants, with the great advantage that neither are foodstuffs, that is to say that there is no competition from food usage, as is the case with Soya, canola, sunflower and other oilseeds.

[0010] In the following a number of documents are cited relating to this technology. Nonetheless, all of these differ in terms of the process and the compounds that are objects of this invention.

[0011] Brazilian patent application PI 0520104-7 concerns a process for preparation of a bio-fuel mixture comprising a fraction of fatty acid alkyl ester and at least one fraction of glycerine containing substituents forming mono and/or diglycerides and/or triglycerides and also a device for preparation of said mixture. The glycerine fraction corresponds to at least 1% by weight of the fuel mixture. The bio-fuel mixture can be used as a fuel in diesel engines without additional cooling, and/or can be added to a conventional diesel fuel mixture.

[0012] Said patent application presents a use that differs from that proposed by the present invention since the use of the castor oil is for the production of bio-fuel while with this invention it is for the production of bio-lubricant. The chemical reactions, despite being transesterification reactions, have reaction conditions, raw materials and catalysts that are different.

[0013] Application MU 8902161-4 concerns the use of Jatropha oil, extracted from the seeds and purified, as a replacement for naphthenic and paraffinic oils, derived from petroleum, as an insulating fluid for high voltage transformers.

[0014] Said application presents a use that differs from that of the present invention. The present invention deals with the synthesis of lubricants from Jatropha oil biodiesel, and not an insulating oil. In addition, in that document the focus is solely on the extraction and purification of vegetable oil and the subsequent mixing with additives, while with the present invention there is a chemical reaction.

[0015] A publication from 2006 (Silva, J. A. C.; *Desenvolvimento de um Lubrificante Biodegradável a partir de Ésteres do Biodiesel da Mamona* [*Development of a biodegradable lubricant from castor bean biodiesel esters*], MSc dissertation, COPPE/UFRJ, Rio de Janeiro, RJ, Brazil), describes a process for the synthesis of bio-lubricants from castor bean ethyl biodiesel by means of chemical catalysis. In this case the raw material, despite deriving from castor beans, uses an ethyl biodiesel and the catalyst is chemical while in the present invention methyl biodiesel is involved and the catalysis is enzymatic. In addition, the process reaction conditions are different from the process conditions of this invention due, for example, to the absence of water.

[0016] The technology developed and described in the present invention has the main benefit that the bio-lubricants obtained from the castor oil methyl biodiesel and the Jatropha oil methyl biodiesel are biodegradable.

[0017] The process for obtaining bio-lubricants obtained from castor oil methyl biodiesel and from Jatropha oil methyl biodiesel, by the enzymatic route, also features:

- a) high selectivity of enzymes;
- b) high yields in the conversion of the esters;

- c) milder reaction conditions, avoiding degradation of the reagents and products;
- d) less energy consumption due to lower temperatures;
- e) biodegradability of the catalyst; and
- f) ease of recovery of the enzymatic catalyst.

[0018] That is to say that the bio-lubricants obtained from castor oil methyl biodiesel and from Jatropha oil methyl biodiesel, by the enzymatic route, represent new products and processes which are important and responsible for the diversification of the line of lubricants previously existing in the market.

BRIEF DESCRIPTION OF THE FIGURES

[0019]

Figures 1A, 1B and 1C show the ricinoleic, oleic and linoleic acids, respectively, in their structural formulas.

Figure 2 shows the transesterification reaction of the methyl ricinoleate (A) with trimethylolpropane (TMP) in the presence of an enzymatic catalyst (C).

Figure 3 shows the transesterification reaction of the methyl oleate (B) with trimethylolpropane (TMP) in the presence of an enzymatic catalyst (C).

DETAILED DESCRIPTION OF THE INVENTION

[0020] The production of bio-lubricants from castor oil methyl biodiesel (methyl ricinoleate) and from Jatropha oil methyl biodiesel (mixture of methyl oleate and linoleate) proposed in the invention takes place through enzymatic catalysis and has as the principal step the transesterification reaction of the biodiesel with a polyhydroxylated alcohol, with subsequent purification and separation of the product: methanol (D) and bio-lubricant (E, F).

REACTION WITH CASTOR OIL METHYL BIODIESEL

[0021] The reaction is performed in batch type reactors, thermostatically controlled and with agitation of 700 rpm. Removal of the alcohol formed as a by-product takes place under a vacuum of 0.01 bar (1 kPa) to increase the reaction conversion.

[0022] A mixture of trimethylolpropane (TMP) (5%- 12% w/w with regard to the weight of the biodiesel plus TMP) and water, in a proportion of 1%- 11 % w/w in relation to the weight of biodiesel plus TMP, is initially added to the reactor. Once the TMP has solubilised in the water, the methyl ricinoleate is added, in a proportion of 77%- 94% w/w in relation to the weight of the biodiesel plus TMP.

[0023] The reaction mixture is heated to a temperature that may vary between 40°C and 55°C, and then the lipase is added, in a proportion of 1%- 4% w/w in relation to the weight of the mixture of biodiesel plus TMP. The system is agitated at 700 rpm and a vacuum of 0.01 bar (1 kPa) is created.

[0024] At the end of the reaction, the reactor is unloaded and the mixture is filtered and centrifuged to separate the enzyme and stored in the freezer at a temperature of -10°C.

[0025] The conversion of the reagent (methyl ricinoleate) into products is calculated on the basis of the disappearance of this, monitored by means of liquid chromatography (HPLC).

[0026] Some reactions are carried out at a pressure of 1 bar (1×10^5 Pa). However, the process takes place in the range of pressures of between 0.01 bar and 1 bar (10^3 and 10^5 Pa).

[0027] The methanol (D) formed is collected during the process by means of a gas condensation system. Separation of the methanol from the reaction medium increases the conversion of the process.

[0028] Figure 2 shows the transesterification reaction of the methyl ricinoleate (A) with the TMP, in the presence of the enzymatic catalyst (C) with methanol (D) and the basic lubricating oil methylolpropane tri-ricinoleate (E) being obtained.

[0029] The following alcohols can be used: TMP, the neopentyl glycol and pentaerithrytol alcohols.

[0030] As enzymatic catalysts (C) the following lipases are used: *Candida rugosa* (Lipomod 34P- Biocatalysts); *Candida antarctica* (Novozym 435- Novozymes) and *Rhizomucor miehei* (Lipozym IM RM- Novozymes). These are all commercial enzymes, with Novozym and Lipozym being immobilised.

[0031] The physico-chemical properties of the lipases and their respective hydrolytic activities, as provided by the manufacturers, are shown in Tables 1, 2 and 3 below.

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Table 1: Typical properties of the enzyme Lipomod 34P (biocatalysts).

TABLE 1	
PROPERTIES	VALUES
Activity	115 000 Lipase U/g (typical) 65 000 Esterase U/g (approx.)
Biological source	Candida rugosa
Form	White powder
Working pH	5-8
Working temperature	40°C - 55°C

Table 2: Typical properties of the enzyme Novozym 435 (Novozymes).

TABLE 2	
PROPERTIES	VALUES
Activity	10 000 Lipase U/g (typical)
Biological source	Candida Antarctica
Form	Immobilised granulate
Working pH	-
Working temperature	-

Table 3: Typical properties of the enzyme Lipozym IM RM (Novozymes).

TABLE 3	
PROPERTIES	VALUES
Activity	150 Esterase U/g (approx.)
Biological source	Rhizomucor miehei
Form	Immobilised granulate
Working pH	-
Working temperature	-

REACTION WITH JATROPHA OIL METHYL BIODIESEL

[0032] The reaction is performed in batch type reactors with agitation at 700 rpm. These reactors have a volume of 50 ml and are thermostatically controlled. When removal of the alcohol formed as a by-product is necessary, the system is placed under a vacuum of 0.01 bar (1 kPa) with the consequence that the conversion is increased.

[0033] Trimethylolpropane- TMP (5%- 12% w/w with regard to the weight of the biodiesel plus TMP) and water, in a proportion of 1%- 11 % w/w with regard to the weight of the biodiesel plus TMP are initially added to the reactor. The reaction temperature is between 40°C and 55°C. The lipase is added when the reactor is at the reaction temperature, in a proportion of 1%- 4% w/w with regard to the weight of reagents: biodiesel plus TMP. Agitation is maintained at a speed of 700 rpm and the pressure in the range 0.01 bar (1 kPa).

[0034] At the end of the reaction, the reactor is unloaded and the mixture is filtered and centrifuged to separate the enzyme and stored at a temperature of- 10°C.

[0035] The conversion of the reagent, methyl oleate, into products is calculated on the basis of the disappearance of that which is monitored by liquid chromatography (HPLC).

[0036] The reactions can occur in a range of pressures of between 0.01 bar and 1 bar (10^3 and 10^5 Pa).

[0037] The methanol (D) formed is collected during the reaction by means of a gas condensation system.

[0038] Figure 3 illustrates the transesterification reaction of the methyl oleate (B) with the TMP, in the presence of

the enzymatic catalyst (C) with methanol (D) and the basic oil methylolpropane trioleate (F) being obtained.

[0039] The neopentyl glycol and pentaerythritol alcohols and the enzymatic catalysts mentioned above are used.

[0040] The following results are obtained:

- conversion of 80% to 99% of the ester (castor oil and Jatropha oil biodiesel);
- viscosity of the bio-lubricant at 100°C: from 6 cSt to 25 cSt;
- viscosity index (VI) of the bio-lubricant: from 120 to 160;
- pour point of the bio-lubricant: from -12°C to -39°C; and
- oxidation stability (RPVOT) of the bio-lubricant: 65 minutes.

[0041] Comparing the results obtained in the present invention with those obtained by chemical catalysis, there is a major improvement in the conversion since with chemical catalysis the conversion is 40% to 50% of the ester (castor oil and Jatropha oil biodiesel).

[0042] The viscosity (VI) and pour point values of the bio-lubricant obtained in the chemical process are equivalent to those of the bio-lubricant obtained in the enzymatic process. But the oxidation stability of the bio-lubricant provides a better result when the catalysis is enzymatic.

[0043] The process developed uses commercial enzymatic catalysts and milder process conditions and in this way makes it possible to obtain bio-lubricants with excellent physico-chemical and performance properties, with less energy expenditure, which makes the process described here viable.

Claims

1. Process for the production of bio-lubricant from methyl biodiesel, **characterised in that** it comprises the steps:

adding the following ingredients in the respective concentrations and order, to the reactor:

- polyhydroxylated alcohol in a range of 5% - 12% w/w with regard to the weight of the biodiesel plus the weight of the alcohol;
- water in a concentration of 1% - 11 % w/w with regard to the weight of biodiesel plus the weight of alcohol;
- methyl biodiesel, in a range of concentration of 77% - 94% with regard to the weight of the biodiesel plus the weight of alcohol, once the polyhydroxylated alcohol has solubilised in the water; and
- enzymatic catalyst, in a proportion of 1% - 4% w/w with regard to the weight of the biodiesel plus the weight of the alcohol;
- agitation of the system preferably by means comprising rotation and preferably at 500 to 900, more preferably 600 to 800 especially about 700 rpm at least at the start of agitation;
- maintaining the reaction temperature at between 40°C - 55°C and the pressure at between 0.01 bar - 1 bar (10^3 and 10^5 Pa);
- monitoring the reaction kinetics preferably by liquid chromatography (HPLC);
- unloading the reactor once the reaction has achieved the desired conversion;
- filtering and/or centrifuging the mixture obtained; and
- storing the purified product preferably at a temperature of -15°C to -5°C, more preferably about -10°C and optionally for further analysis.

2. Process for the production of bio-lubricant from methyl biodiesel, according to claim 1, **characterised in that** the polyhydroxylated alcohol is trimethylolpropane (TMP), neopentyl glycol or pentaerythritol.

3. Process for the production of bio-lubricant from methyl biodiesel, according to claim 1, **characterised in that** the methyl biodiesel is methyl ricinoleate and/or methyl oleate and/or a mixture of these reagents in any proportion.

4. Process for the production of bio-lubricant from methyl biodiesel, according to claim 1, **characterised in that** the enzymatic catalyst is a lipase.

5. Process for the production of bio-lubricant from methyl biodiesel, according to claim 4, **characterised in that** the lipase is *Candida rugosa*, *Candida antarctica* and *Rhizomucor miehei*.

6. Process for the production of bio-lubricant from methyl biodiesel, according to claims 1, 2, 3, 4 and 5, **characterised in that** the reaction is performed in batch type reactors, thermostatically controlled and with agitation of 700 rpm.

7. Process for the production of bio-lubricant from methyl biodiesel, according to claims 1, 2, 3, 4, 5 and 6, **characterised in that** the conversion of castor oil or Jatropa oil biodiesel is 80% to 99%.

8. Process for the production of bio-lubricant from methyl biodiesel, according to claims 1, 2, 3, 4, 5, 6 and 7, **characterised in that** when the polyhydroxylated alcohol is trimethylolpropane (TMP) and the methyl biodiesel is methyl ricinoleate, the product obtained is methylolpropane tri-ricinoleate (E).

9. Process for the production of bio-lubricant from methyl biodiesel, according to claims 1, 2, 3, 4, 5, 6 and 7, **characterised in that** when the polyhydroxylated alcohol is trimethylolpropane (TMP) and the methyl biodiesel is methyl oleate, the product obtained is methylolpropane tri-oleate (F).

10. Compound obtained by the process, as defined in claim 8, **characterised by** it being methylolpropane tri-ricinoleate (E) with a:

- viscosity at 100°C of 6 cSt to 25 cSt;
- viscosity index (VI) of 120 to 160;
- pour point of -12°C to -39°C; and
- oxidation stability (RPVOT) of 65 minutes.

11. Compound obtained by the process, as defined in claim 9, **characterised by** it being methylolpropane tri-oleate (F) with a:

- viscosity at 100°C of 6 cSt to 25 cSt;
- viscosity index (VI) of 120 to 160;
- pour point of -12°C to -39°C; and
- oxidation stability (RPVOT) of 65 minutes.

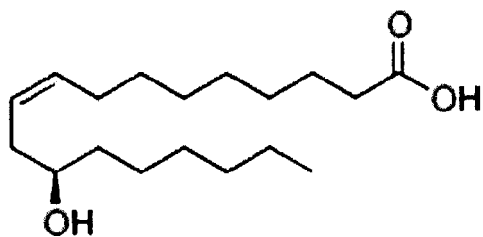


FIGURE 1A

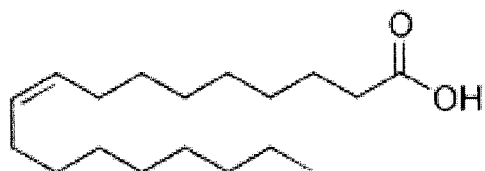


FIGURE 1B

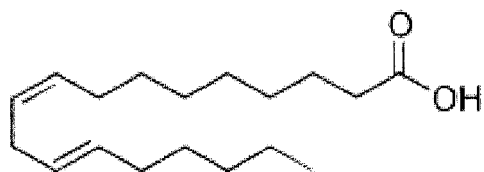
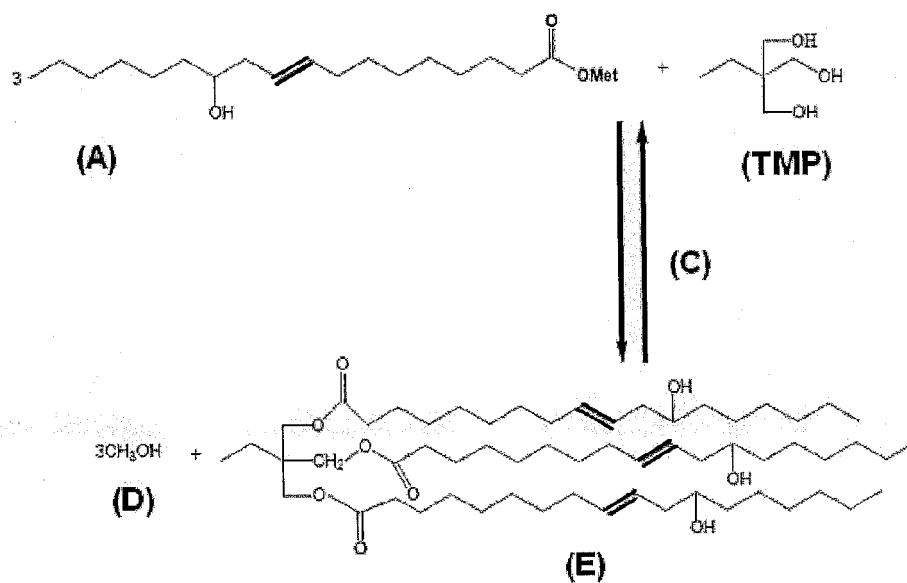
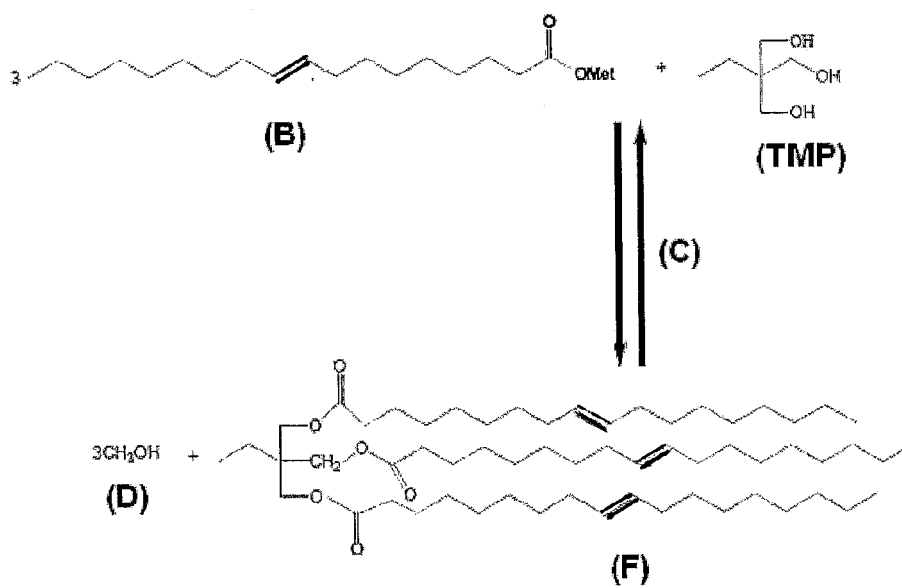


FIGURE 1C

**FIGURE 2****FIGURE 3**



EUROPEAN SEARCH REPORT

Application Number
EP 13 16 4145

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 20 June 2013	Examiner Klaes, Daphne
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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