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(54) Title: NEW PROCESS FOR PRODUCING ESTERS FROM VEGETABLE OILS AND/OR ANIMAL FATS BY USING HETEROGENEOUS CATALYSTS, PARTICULARLY IN THE PRESENCE OF FREE ACIDITY AND WATER

(57) Abstract: A process for producing esters from vegetable oils or animal fats, comprising the step of esterification and/or transesterification reaction of vegetable oils and/or animal fats with at least one aliphatic alcohol in the presence of heterogeneous catalysts, the esterification and/or transesterification reaction occurring in the presence of a dialkyl carbonate.

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NEW PROCESS FOR PRODUCING ESTERS FROM VEGETABLE OILS AND/OR ANIMAL FATS BY USING HETEROGENEOUS CATALYSTS, PARTICULARLY IN THE PRESENCE OF FREE ACIDITY AND WATER

5 **Technical field**

The present invention relates to a process for producing esters from vegetable oils and animal fats, particularly for producing biodiesel, which uses heterogeneous esterification and transesterification catalysts to produce esters by a reaction between vegetable oils or animal fats, aliphatic alcohols
10 and dialkyl carbonates.

Background art

Biodiesel, used as fuel in diesel engines, is constituted by a mixture of esters of fatty acids obtained by transesterification reaction of vegetable oils and animal fats with methanol or ethanol and subsequent separation from
15 glycerin.

The transesterification reaction for producing biodiesel is performed generally by using as catalysts bases of alkaline metals such as for example NaOH, KOH, NaOCH₃, KOCH₃ (1, 2).

S. Gryglewicz (3) has performed transesterification tests with MgO, Ca(OH)₂, CaO, Ca(CH₃O)₂, Ba(OH)₂ > NaOH, and has found the following
20 scale of activity: NaOH > Ba(OH)₂ > Ca(CH₃O)₂ > CaO, while magnesium oxide and calcium hydroxide have shown no activity at the boiling point of methanol.

Barium hydroxide dissolves, producing a substantially homogeneous
25 catalyst, while calcium oxide produces suspensions (3). Suspensions of CaO make it difficult to separate the ester and glycerin phases.

Stern et al. (4) have proposed catalysts based on zinc oxide and zinc aluminate in the crystalline form of spinel, which have been found to be active at high temperatures (T 225°C) in the transesterification reaction of
30 oils with methanol.

However, these catalysts are sensitive to the presence of water and exhibit the best performance for water contents below 1000 ppm (5).

Leclercq et al. (6) have found that magnesium oxide and mixed magnesium-aluminum oxides are active in the transesterification of oils at the reflux temperature of methanol, but the conditions used (methanol/oil molar ratio = 275-75) and the reaction time (22 hours) required in order to have high conversions do not allow industrial use of this process.

Suppes et al. (7) have found that catalysts based on zeolite NaX and ETS-10 are active in the transesterification reaction at temperatures below 125 °C. The activity of these catalysts, however, is compromised by the presence of free acidity.

In recent years it has been found that heterogeneous catalysts constituted by vanadyl phosphate dihydrate are active in partial oxidation reactions of hydrocarbons (8, 9). Vanadyl phosphates substituted with an M^{3+} cation and supported on titania and silica have been tested in the partial oxidation reaction of propane (10). These catalysts, in addition to having remarkable redox properties, also have interesting Bronsted and Lewis acid properties.

Disclosure of the Invention

The aim of the present invention is to provide a process which allows to produce biodiesel at lower costs than known processes even starting from oils which contain high free acidity and in the presence of water even derived from the esterification reaction.

An object of the present invention is to provide a process which has additional economic advantages, allowing to produce the byproduct of biodiesel, glycerin, with a higher degree of purity and therefore with a lower production cost.

Another object of the present invention is to provide a process in which the formation of surfactant species in solution, which by facilitating the formation of emulsions slow the step for separation of the glycerin and

biodiesel, is limited, avoiding the need to neutralize the products and further avoiding the need for an operation for separating the glycerin from the residues of the homogeneous catalyst.

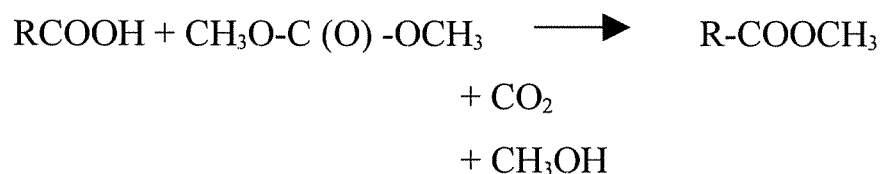
Further objects will become apparent from the following detailed
5 description of the invention.

This aim and these objects are achieved with a process according to the present invention, which provides for the use of heterogeneous catalysts to produce esters, particularly biodiesel, by reaction between vegetable oils or animal fats and aliphatic alcohols with heterogeneous esterification and
10 transesterification catalysts in the presence of dialkyl carbonates, particularly dimethyl carbonate, and aliphatic alcohols, particularly methanol.

The process according to the present invention comprises in particular, among its stages, the mixing of vegetable oils or animal fats with
15 aliphatic alcohols containing dialkyl carbonate, particularly dimethyl carbonate or diethyl carbonate, in a quantity which is at least stoichiometric with respect to the water plus the acid that is present in the mix, placing the mix in contact with the catalyst, and then heating to the reaction temperature.

20 The dimethyl carbonate has two main functions:

- Reacting with the free acid to provide the methyl ester without forming water.



25

- Reacting with the water that is present in the system to yield CH_3OH and CO_2



Ways of carrying out the invention

30 In one embodiment, the reaction stage of the process according to the

present invention comprises the steps of:

- mixing vegetable oils or animal fats with aliphatic alcohol, obtaining a mixture of vegetable oils and/or animal fat and aliphatic alcohol, and dialkyl carbonate, particularly dimethyl carbonate or diethyl carbonate;
- placing said heated mix in contact with said catalyst; and
- heating said mix.

The alcohol used can be for example an aliphatic monoalcohol, particularly an aliphatic monoalcohol which contains 1 to 5 carbon atoms, for example methanol or ethanol.

The heterogeneous catalyst used in the process according to the present invention can be a heterogeneous catalyst for the esterification and transesterification reaction of vegetable oils or animal fats, for example a heterogeneous catalyst selected from the group consisting of vanadyl phosphate dihydrate, supported TiO_2 , hydrotalcites, sulfuric acid, p-toluenesulfonic acid, styrene-based sulfonic resins, et cetera.

The process according to the present invention can be performed at a temperature which is suitable for the reaction, for example at a temperature from 50 to 200 °C, in particular at a temperature around 60-120 °C.

The weight ratio of alcohol/vegetable oil or animal fat used in the process according to the present invention is comprised for example from 0.5 and 5.

Moreover, in one embodiment of the process according to the present invention, the reaction occurs in the presence of free fatty acids, even in high concentrations, for example higher than 10%.

Moreover, in the process according to the present invention, the reaction can occur discontinuously or continuously.

The dialkyl carbonate is used in a quantity which is at least stoichiometric with respect to the sum of the acidity that is present in the oil and of the water that is present in the system.

In the process according to the present invention, after the reaction, the heterogeneous catalysts can be separated by filtration, the unreacted aliphatic alcohol can be separated by distillation, and the glycerin phase can be separated by decantation from the ester phase.

- 5 The process according to the present invention can also comprise a further stage of transesterification of the unreacted glycerides that are present in the ester phase.

In the process according to the present invention, the reaction can be performed discontinuously or in continuous reactors, both of the agitated
10 type and of the fixed-bed type.

The process according to the present invention allows cost reduction and allows to work in continuous plants.

The following examples are suitable for the purpose of illustrating the invention and should not be considered as limiting its scope.

- 15 All the reagents used were supplied by FLUKA, except for the soybean oil, supplied by Casa Olearia Italiana S.p.A. (Monopoli, BA). The process according to the invention consists in mixing vegetable oils or animal fats with an aliphatic alcohol, preferably methanol and dialkyl carbonate, particularly dimethyl carbonate. The reaction mix is then heated
20 to the reaction temperature and placed in contact with the catalyst.

Example 1 – Esterification of acid oil in the presence of acid resin and methanol at 70 °C

a) Test conducted with acid resin and methanol at 70 °C

- 25 An esterification test was conducted by using 25% OA acid oil, a dry polystyrene-based sulfonic acid exchange resin (Resindion CFS/MB; 15% by weight with respect to the oil) in the presence of methanol (15% by weight with respect to the weight of the oil).

The dry resin, dried beforehand in a stove at a temperature of 100 °C, and the methanol were added to the oil, which was initially homogenized
30 and heated to a temperature of approximately 40 °C. The reaction occurred

at the boiling point of methanol, 70 °C.

As can be seen in table 1, acidity dropped to 1.1% in 150 minutes, yielding 95.6% conversion.

5 Table 1
Esterification with methanol and acid resin

Time (min)	Acidity (% OA)*	Conversion
0	25	0
150	1.1	95.6

*Acidity expressed as a percentage of oleic acid (OA).

10 The presence of water, formed during the esterification reaction, prevents the complete elimination of acidity.

b) Test conducted with acid resin used previously and methanol at 70 °C

The test was subsequently repeated by using the same catalyst as in
15 the preceding test in order to assess its catalytic activity and its lifespan.

The results shown in table 2 illustrate a clear loss of catalytic activity.

Table 2
Esterification with methanol and previously used acid resin

20

Time (min)	Acidity (% OA)*	Conversion
0	25	0
150	5	80

c) Test conducted with humid acid resin and methanol at 70 °C

An esterification test was conducted on a 19.43% acid oil, using a humid resin (15% by weight with respect to the oil) and methanol (10% by
25 weight with respect to the oil).

As shown in table 3, the reaction has long times and acidity is not eliminated completely.

Table 3. Esterification with methanol and humid resin

Time (h)	Acidity (% OA)*	Conversion
0	19.43	0
38	2.11	89.14

5

The previous tests were subsequently conducted in the presence of dimethyl carbonate in order to check the performance of this compound in the esterification reaction.

10 Example 2 - Esterification of acid oil in the presence of acid resin, dimethyl carbonate and methanol as cosolvent at 70 °C.

a) Test conducted with acid resin, dimethyl carbonate and methanol at 70 °C

15 An esterification test was conducted by using 18.8% OA acid oil, an acid resin (15% by weight with respect to the oil) and dimethyl carbonate (stoichiometric ratio equal to the ratio of the acid) and methanol as cosolvent (15% by weight with respect to the weight of the oil). As can be seen in table 4, in 150 minutes of reaction the acidity dropped to 0.6 per cent, giving a 96.8% conversion.

20 Table 4

Esterification with acid resin, dimethyl carbonate and methanol

Time (min)	Acidity (% OA)*	Conversion
0	18.8	0
120	0.6	96.8

25 By comparing table 4 with table 1, one can say that the presence of dimethyl carbonate in the reaction system improves the performance of the

resin and allows the almost complete elimination of acidity.

b) Test conducted with acid resin, dimethyl carbonate and methanol at 100 °C

The esterification test was conducted at 100 °C to assess the influence
5 of the temperature on the elimination of acidity.

An oil with an acidity of 18% received the addition of dry resin (15%
by weight with respect to the oil), excess dimethyl carbonate (the moles of
added dimethyl carbonate were twice those of the acid) and methanol as a
cosolvent (2% by weight with respect to the oil). Final acidity after 150
10 minutes was 0.57%.

The reaction performed at the temperature of 100 °C did not appear to
yield substantial differences with respect to the reaction conducted at 70 °C.
The conversion was practically the same (96.7%).

b) Test conducted with previously used acid resin and methanol at 70
15 °C.

The resin already used in the preceding reaction was used to check its
activity in the presence of dimethyl carbonate. As can be seen in table 5, the
resin did not deactivate in the presence of dimethyl carbonate and acidity
dropped from 18.8% to 0.6% as in the preceding test (table 4).

20 Table 5

Esterification with acid resin, dimethyl carbonate and methanol

Time (min)	Acidity (% OA)*	Conversion
0	18.8	0
120	0.6	96.8

c) Test conducted with humid acid resin and methanol at 70 °C.

25 An esterification test was conducted on a 19.43% acid oil by using a
humid resin (15% by weight with respect to the oil), dimethyl carbonate (the
moles of which are equal to those of the acid plus those that correspond to a

water content of the resin equal to 50% of its weight) and methanol (10% by weight with respect to the oil).

As in the preceding test, table 3, the reaction times are long, but as can be seen from table 6, acidity drops from 19.43% to 1%.

- 5 This time also, the dimethyl carbonate has improved the performance of the resin, ensuring a greater elimination of the acidity of the system.

Table 6

Esterification with dimethyl carbonate, methanol and humid resin

Time (h)	Acidity (% OA)*	Conversion
0	19.43	0
38	1.1	94.33

10

Example 3 - Esterification of acid oil in the presence of the catalyst vanadyl phosphate dihydrate, $\text{VOP}_4 \cdot 2 \text{H}_2\text{O}$, methanol and dimethyl carbonate.

- 15 The catalyst is prepared as described in WO2007062825 that is incorporated herein by reference.

An esterification test was conducted on a 10.50% OA acid oil in the presence of vanadyl phosphate, by loading a small steel reactor with 2 g of soybean oil, 0.9 g of methanol, 0.1 g of catalyst and a quantity of dimethyl carbonate equal to the moles of acid.

- 20 In the test conducted in WO2007062825, it is noted that the vanadyl phosphate dihydrate used as a catalyst is active in the reaction for transesterification of soybean oil, exhibiting a methyl ester yield of 75.18% in the absence of free acidity and of 78.26% in the presence of acidity (see WO2007062825).

- 25 Moreover, this catalyst acts on the elimination of acidity of the system. Acidity in fact drops from 10.50% to 2.64% (table 7).

The same test was conducted in the presence of dimethyl carbonate,

the moles of which were the same as those of the acid, and the final acidity of the system was 0.5% (table 8).

Table 7

Esterification with vanadyl phosphate and methanol

5

Catalyst	Initial acidity	Conversion
VOP ₄ • 2 H ₂ O	10.50	0
VOP ₄ • 2 H ₂ O	2.64	74.85

Table 8

Esterification with dimethyl carbonate, vanadyl phosphate and methanol

10

Catalyst	Acidity (OA%)	Conversion
VOP ₄ • 2 H ₂ O	10.50	0
VOP ₄ • 2 H ₂ O	0.5	95.23

Example 4 – Esterification of acid oil in the presence of TiO₂/SiO₂, methanol and dimethyl carbonate.

The powdered catalyst TiO₂/SiO₂, the synthesis of which is given in
15 WO2006094986 that is incorporated herein by reference, is acidified with stearic acid. In WO2006094986, conversion in the presence of a free acidity of 5% in OA is assessed.

Free acidity has an only partial effect on the catalyst, reducing its activity by approximately 27%. The resulting conversion is determined by
20 using H-NMR.

Table 9

Catalytic tests in the presence of free acidity

Catalyst	Acidity (SA%)**	Methyl ester yield (%)
TiO ₂ /SiO ₂	0	64
TiO ₂ /SiO ₂	5	46.33

25 **Acidity expressed as a percentage of stearic acid (SA).

The same test was conducted by loading a small steel reactor with 2 g of soybean oil, with 5% acidity, 0.9 g of methanol, 0.1 g of catalyst, and a quantity of dimethyl carbonate equal to the moles of acid.

30 As can be deduced from the table that follows, the presence of dimethyl carbonate improves the methyl ester yield, providing a 64% conversion which is practically the same conversion obtained in the absence of free acidity.

Table 10

35 Catalytic tests in the presence of dimethyl carbonate

Catalyst	Acidity (SA%)**	Methyl ester yield (%)
TiO ₂ /SiO ₂	0	64
TiO ₂ /SiO ₂	5	64

CLAIMS

1. A process for producing esters from vegetable oils or animal fats, comprising the step of esterification and/or transesterification reaction of vegetable oils and/or animal fats with at least one aliphatic alcohol in the
5 presence of heterogeneous catalysts, characterized in that said esterification and/or transesterification reaction occurs in the presence of a dialkyl carbonate.

2. The process according to claim 1, characterized in that it comprises the step of mixing said vegetable oils and/or animal fats with said aliphatic
10 alcohol containing dialkyl carbonate, obtaining a mix of vegetable oils and/or animal fats, aliphatic alcohols and dialkyl carbonate.

3. The process according to claim 2, characterized in that said mix contains water and/or acids, before the reaction.

4. The process according to claim 3, characterized in that said acid is
15 present at a concentration of more than 1% by weight, expressed as oleic acid.

5. The process according to one of claims 3 or 4, characterized in that said dialkyl carbonate is present in a quantity which is at least stoichiometric with respect to the water and the acid that are present in the
20 mix.

6. The process according to claim 2 or 3, characterized in that said mix is placed in contact with said catalyst and is then heated.

7. The process according to claim 6, characterized in that said mix is heated to a temperature between 50 and 200 °C, particularly between 60 and
25 120 °C.

8. The process according to one or more of the preceding claims, characterized in that said dialkyl carbonate is selected from dimethyl carbonate and diethyl carbonate.

9. The process according to one or more of the preceding claims,
30 characterized in that said aliphatic alcohol is an aliphatic alcohol with 1 to 5

carbon atoms, particularly methanol or ethanol.

10. The process according to any one of the preceding claims, characterized in that said aliphatic alcohol and said vegetable oil and/or animal fat are present in a weight ratio from 0.5 to 10.

5 11. The process according to one of the preceding claims, characterized in that it is performed continuously or discontinuously, particularly in agitated or fixed-bed reactors.

12. The process according to any one of the preceding claims, characterized in that after the reaction said heterogeneous catalysts are
10 separated, particularly by filtration.

13. The process according to any one of the preceding claims, characterized in that after the reaction said aliphatic alcohols, if they have remained unreacted, are separated, particularly by distillation.

14. The process according to any one of the preceding claims,
15 characterized in that after the reaction a glycerin phase is separated, particularly by decantation.

15. The process according to any one of the preceding claims, characterized in that said heterogeneous catalyst is selected from the group consisting of a vanadyl phosphate dihydrate, supported TiO_2 , hydrotalcites,
20 sulfuric acid, p-toluenesulfonic acid and styrene-based sulfonic resins and mixed oxides of magnesium and aluminum.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP2008/058030

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11C3/00

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

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, WPI Data, FSTA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/274065 A1 (PORTNOFF MARC A [US] ET AL) 15 December 2005 (2005-12-15) the whole document	1-15
A	US 2002/035282 A1 (SUPPES GALEN J [US]) 21 March 2002 (2002-03-21) the whole document	1-15
A	WO 2007/062825 A (ASER S R L [IT]; SANTACESARIA ELIO [IT]; MINUTILLO GIUSEPPE [IT]; DI S) 7 June 2007 (2007-06-07) cited in the application the whole document	1-15

☐

Further documents are listed in the continuation of Box C.

☒

See patent family annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *P* document published prior to the international filing date but later than the priority date claimed

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- *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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 2005274065	A1	15-12-2005	AU	2005257987 A1		05-01-2006
			BR	PI0403235 A		31-01-2006
			CN	101014562 A		08-08-2007
			EP	1765762 A2		28-03-2007
			EP	1964830 A2		03-09-2008
			JP	2008502780 T		31-01-2008
			KR	20070041518 A		18-04-2007
			WO	2006002087 A2		05-01-2006
US 2002035282	A1	21-03-2002	US	2003149289 A1		07-08-2003
WO 2007062825	A	07-06-2007	NONE			