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Method and system for the esterification of fatty acids

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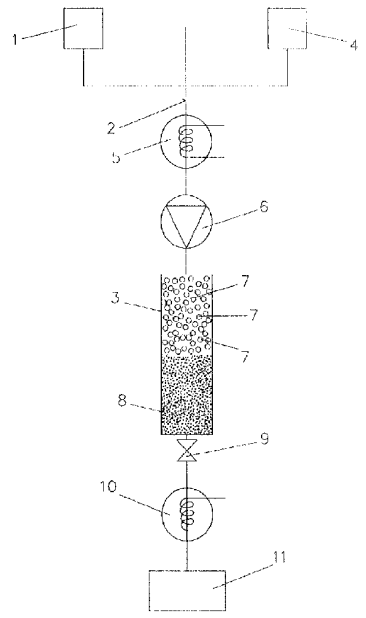
(54) Title: METHOD AND SYSTEM FOR THE ESTERIFICATION OF FATTY ACIDS

(54) Bezeichnung: VERFAHREN UND ANLAGE ZUR VERESTERUNG VON FETTSÄUREN



(57) Abstract: The invention relates to a method and system for the esterification of fatty acids and/or fatty acids contained in fats and oils with low monovalent alcohols, especially methanol. Acids, especially sulphuric acid, dissolved in lower alcohols, especially methanol and/or exclusively in lower alcohols, especially in methanol with ion exchange resins, are added to the fatty acids. The interphases of the mixtures are increased in the reaction section (3) by means of high or strong dynamic shearing cutting forces and/or turbulence. The esterification begins at high pressure and the pressure is reduced during esterification, whereby the pressure loss maintains a high interphase. Said reaction is carried out in the reaction section (3) at a high temperature.

(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren und eine Anlage zur Veresterung von Fettsäuren und/oder von in Fetten und Ölen enthaltenen Fettsäuren mit niederen einwertigen Alkoholen, insbesondere Methanol. Die Fette werden mit Säure, beispielsweise Schwefelsäure, gelöst in niederen Alkoholen, insbesondere in Methanol und/oder nur in niederen Alkoholen, insbesondere in Methanol mit Ionentauscherharzen versetzt. In einer Reaktionsstrecke (3) werden die Phasengrenzflächen der Mischung durch hohe bzw. starke, dynamische Scherkräfte und/oder Turbulenzen vergrössert. Die Veresterung beginnt unter hohem Druck und der Druck wird während der Veresterung abgebaut, wobei der Druckverlust eine hohe Phasengrenzfläche aufrecht hält. Diese Reaktion wird in der Reaktionsstrecke (3) bei hoher Temperatur durchgeführt.

RU, SC, SD, SE, SG, SK (Gebrauchsmuster), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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— *mit internationalem Recherchenbericht*

— *vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen*

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

Method and System for the Esterification of Fatty Acids

The invention relates to a method for the esterification of fatty acids and/or fatty acids contained in fats and oils with low monovalent alcohols, especially methanol, whereby the fatty acids with strong mineral acids, such as sulphuric acid, dissolved in lower alcohols, especially in methanol and/or exclusively in lower alcohols, especially in methanol, are compounded with acid ion exchanger resins. Furthermore, the invention relates to a system for the implementation of said method.

From the textbooks for organic-preparatory chemistry, such as „Organikum", 13th ed.,1974 page 441 et seq. or Weygand/Hilgetag, „Organisch- Chemische Experimentierkunst, 4th ed., 1970, page 377 et seq., it is known that carboxylic acid esters or fatty acid esters may be esterified by esterification of the free acids with lower alcohols, preferably at the temperature of ebullition of the alcohols in presence of strong acids, such as hydrogen chloride, sulphuric acid or sulphonic acids.

A method for the esterification of a fatty acid/fatty acid ester mixture, isolated from the "glycerine phase", is described in EP 708 813 A, whereby the free fatty acids obtained from the neutralisation of the "glycerine phase" are heated to a temperature of 85 °C for two hours, with methanol and concentrated sulphuric acid acting as a catalyst, whereby the content of free fatty acids decreases from about 50 % to 12.5 % and whereby the entire mixture is supplied without any further treatment to an alkali-catalysed transesterification and the catalyst acid is exported through the transesterification process.

Further methods for the esterification of free fatty acids are described in EP 127 104 A, EP 184 740 A and US 4 164 506 A, whereby the free fatty acids are present in a mixture with fatty acid triglycerides and the esterification is carried out by means of heating with methanol at 65 °C, whereby sulphuric acid or a sulphonic acid act as a catalyst.

The serious disadvantage of all these known methods lies in the fact, however, that the esterification step requires an enormous amount of time. Thus, as a rule said kind of esterification requires stirring over a period of two to three hours.

The object of the present invention is to provide a method of the above-mentioned type which allows a rational production in an economically acceptable system, preferably in an industrial-sized system, but is also economic in small systems.

Said object is fulfilled by the invention.

The method according to the invention is characterised in that in a reaction section the interphases and boundary surfaces respectively of the mixture are increased by means of high or powerful dynamic shearing forces and/or turbulence, whereby the esterification starts under a high pressure and the pressure is reduced during esterification, whereby the pressure loss maintains a high interphase, and in that said reaction is carried out in the reaction section at a high temperature.

The present invention allows for the first time to provide a pre-product for the production of bio-diesel by means of base-catalysed transesterification. Thus, the possibility is provided to produce diesel fuel, so-called eco-diesel or bio-

diesel, in ecologically optimal conditions of production while maintaining all the advantages thereof. With this invention positive economic and ecological arguments are provided, which will stimulate a more intensive discourse on the role of renewable energy and resources.

Another surprising advantage results from the invention, namely in the field of waste management or hazardous waste disposal. With this invention it is also possible to recycle and reuse used table oil ecologically, even if said oil has a high content of fatty acids. The use of used table oil in the method according to the invention is possible without reservations due to the high purity of the end products.

The present invention makes it possible to accelerate the reaction through the enlargement of the interphases and through dynamic processes during the transesterification. Due to the high and powerful dynamic turbulence respectively, the size of the drops in the liquid phases is effectively reduced, so that much smaller drops are produced, resulting in a much larger surface, which means that the chemical balance state is reached faster. Reaching the chemical balance state may take less than a minute. This means an enormous shortening of the reaction time. However, said method according to this invention is not suited for the so-called sedimentation method, since the sedimentation times would be too long due to the fine distribution of the drops.

According to a special feature of the invention, the pressure at the beginning of the reaction section lies at 2 to 500 bar, in particular at 50 to 200 bar and most preferably between 70 and 150 bar. The advantage thereby is that due to the high pressure the methanol remains liquid.

In accordance with a further particular feature of the invention, the reaction is carried out in the reaction section at a temperature of 50 to 300 °C, in particular at 80 to 150 °C. Due to the high temperature, the high reaction rate is reached in an advantageous manner.

According to an embodiment of the invention, the high shear forces and powerful dynamic turbulence respectively are produced by mechanical devices. Said type of devices is easy to install and therefore does not require much maintenance during operation. The turbulence is created primarily by the rapid flow of the mixture around said devices. Moreover, such a reactor is inexpensive and extremely compact.

According to another embodiment of the invention the large interphases are created by ultrasound. Integrating an ultrasound device has proven to be advantageous, since the transesterification can therewith be specifically accelerated through large interphases. According to another special feature of the invention, the reaction section is followed by a non-turbulent post-reaction section. By means of the residence time of the reaction mixture in the post-reaction section, an increase of the esterification degree is obtained.

According to one embodiment of the invention, in the post-reaction section a pressure, preferably the initial pressure of the reaction section, is maintained or possibly further reduced. Maintaining the pressure also contributes to the improvement of the esterification degree. According to specific parameters in the esterification process, however, a further reduction of pressure may also be of advantage.

According to a special further development of the invention, the post-reaction section is filled with strong-acid ion

exchangers. In a process implementation with ion exchangers, the compounding of the fats with acids is omitted in a known manner. Also with such a process an optimal esterification process is achieved.

It is also an object of the invention, however, to provide a system for the implementation of said method.

The system according to the invention is characterised in that the reaction section is a pipe filled with balls of the same size or different sizes and/or possibly has devices such as baffles, propellers or the like. The advantageous turbulence is created primarily by the rapid flow of the mixture around the balls or devices.

In accordance with another embodiment of the invention, an ultrasound device is provided in the reaction section. The integration of an ultrasound device has proven advantageous, since therewith the transesterification can be specifically accelerated through large interphases.

According to a further embodiment of the invention, the reaction section is preceded by a heater, and a cooler possibly follows the reaction section or the post-reaction section. By means of the heater, the reaction mixture can be brought to the desired high temperature and can be cooled down with the cooler according to the parameters for the process.

According to a further development of the invention, a pump, in particular a high-pressure pump, is provided to introduce the liquid into the reaction section. The integration of a high-pressure pump has proven advantageous because the turbulence achieves high dynamics and thus a large interphase for the transesterification.

The invention will now be explained in more detail based on an embodiment which is illustrated in the drawing.

The Fig. schematically shows a system for the implementation of the method for the esterification of fatty acids.

According to the Fig., the raw material, such as higher, saturated and/or unsaturated fats of vegetable and/or animal origin, containing free fatty acids, flows into a supply line 2 leading to a reaction section 3. The method is particularly suitable for fats having a higher or high content, preferably more than 5 %, of free fatty acids. Said method may, for example, be used with the production of fatty acid methyl ester, whereby a high profitability can be guaranteed.

Naturally, the method may also be used with pure fatty acids.

The lower alcohol, in particular methanol, is pumped into the supply line 2 leading to the reaction section 3 together with the acid, in particular sulphuric acid.

Said reaction mixture 3 is brought to the corresponding temperature by a heater 5 which is arranged before the reaction section 3. The reaction in the reaction section 3 is carried out at a temperature of 50 to 300 °C, in particular at a temperature of 80 to 150 °C.

Said heated reaction mixture is introduced into the reaction section 3 via a high-pressure pump 6. In the reaction section 3 the reaction mixture is exposed to high shear forces, whereby powerful dynamic turbulence is produced. This results in the interphases of the reaction mixture becoming immensely enlarged. The high shearing forces or the powerful dynamic

turbulence are created by mechanical devices in the reaction section 3.

The mechanical devices in the reaction section 3 may be balls 7 of the same size or different sizes. However, it is also possible to provide, possibly in addition, devices such as baffles, propellers or the like.

The enlargement of the interphases of the reaction mixture may also be achieved by an ultrasound device. Of course, said device may also be provided in addition to the mechanical devices.

Due to the high and powerful dynamic turbulence respectively, the size of the drops in the liquid phases is effectively reduced, so that much smaller drops are produced, resulting in a much larger surface, which means that the chemical balance state is reached faster. Reaching the chemical balance state may take less than a minute. This means an enormous shortening of the reaction time.

In the reaction section 3 part of the pressure that is present at the beginning of the reaction section 3 is reduced.

In order to increase the esterification degree, the reaction section 3 may be followed by a non-turbulent post-reaction section 8 which, possibly under the initial pressure of the reaction section 3, calms down the reaction mixture. For this purpose, the post-reaction section 8 is provided with a pressure keeping valve at its end. If this should prove to be more advantageous for the procedure of the process, pressure may also be reduced in the post-reaction section 8.

According to an alternative procedure of the process without the addition of acid, in particular sulphuric acid, at the beginning of the reaction section 3, there is provided a strong-acid ion exchanger, in particular an ion exchanger resin, in the post-reaction section 8.

The post-reaction section 8 is followed by a cooler 10, which cools down the reaction mixture correspondingly, before it is collected in a container 11 for further processing.

In conclusion, it must be pointed out that for better legibility the individual components and assemblies in the drawing are not shown proportionally or to scale.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

Numerous variations and modifications will suggest themselves to persons skilled in the relevant art, in addition to those already described, without departing

from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the above description.

2003218521 30 Mar 2009

CLAIMS:

1. A method for the esterification of fatty acids with low monovalent alcohols with 1 to 4 carbon atoms, comprising the steps of dissolving the fatty acids in low monovalent alcohols with 1 to 4 carbon atoms, combining the resulting solution with a strong mineral acid and acid ion exchanger resins in a reaction section (3) to form a mixture, starting esterification of the mixture at an initial pressure of 2 to 500 bar and reducing said pressure during the esterification whereby the pressure reduction reduces the drop size in the liquid phases of the mixture, the esterification being carried out in the reaction section (3) at a temperature of 50°C to 180°C, characterized in that dynamic shear forces and/or turbulence in the reaction section (3) reduce the drop size in the liquid phases of the mixture thereby shortening reaction time of the esterification.

2. The method according to claim 1, characterized in that the fatty acids comprise fatty acids contained in fats and oils.

3. The method according to claim 1 or claim 2, characterized in that the alcohol is methanol.

4. The method according to any one of the preceding claims, characterized in that the strong acid is sulphuric acid.

5. The method according to any one of the preceding claims, characterized in that the initial pressure in the reaction section (3) is 5 to 200 bar.

6. The method according to any one of the preceding claims, characterized in that the initial pressure in the reaction section (3) is 70 to 150 bar.

7. The method according to any one of the preceding claims, characterized in that the shearing forces and the dynamic turbulence respectively are produced by mechanical devices in the reaction section (3).

8. The method according to any one of the preceding claims, characterized in that dynamic turbulence in the reaction section (3) is created by ultrasound.

9. The method according to any one of the preceding claims, characterized in that the mixture passes from the reaction section (3) to a non-turbulent post-reaction section (8).

10. The method according to claim 9, characterized in that the pressure of the reaction section (3) is maintained in the post-reaction section (8).

11. The method according to claim 9, characterized in that the pressure of the reaction section (3) is reduced in the post-reaction section (8).

12. The method according to claim 9, characterized in that the pressure from the reaction section (3) is

maintained at the initial pressure of the reaction section (3) in the post-reaction section (8).

13. The method according to claim 12, characterized in that the pressure in the post-reaction section (8) is further reduced.

14. The method according to any one of claims 9 to 13, characterized in that the post-reaction section (8) is filled with strong-acid ion exchangers.

15. A system when used to perform the method according to any one of claims 1 to 4, comprising a reaction section (3) provided with mechanical devices capable of producing dynamic shear forces and/or turbulence in a mixture contained in the reaction section (3) so as to reduce drop size in the liquid phases of the mixture in said reaction section (3), a pump for introducing liquid into the reaction section (3), and a post-reaction section (8).

16. The system according to claim 15, characterized in that the reaction section (3) is a pipe filled with balls (7) of the same size or different sizes and/or baffles, propellers and the like.

17. The system according to claim 15 or 16, whereby the pump is a high-pressure pump (6).

18. The system according to any one of claims 15 to 17, characterized in that an ultrasound device is provided in the reaction section (3).

19. The system according to any one of claims 15 to 18, characterized in that the reaction section (3) is preceded by a heater (5), and the reaction section (3) or the post-reaction section (8) is followed by a cooler (10).

20. A system for performing a method for the esterification of fatty acids with low monovalent alcohols with 1 to 4 carbon atoms substantially as hereinbefore described with reference to the Figure.

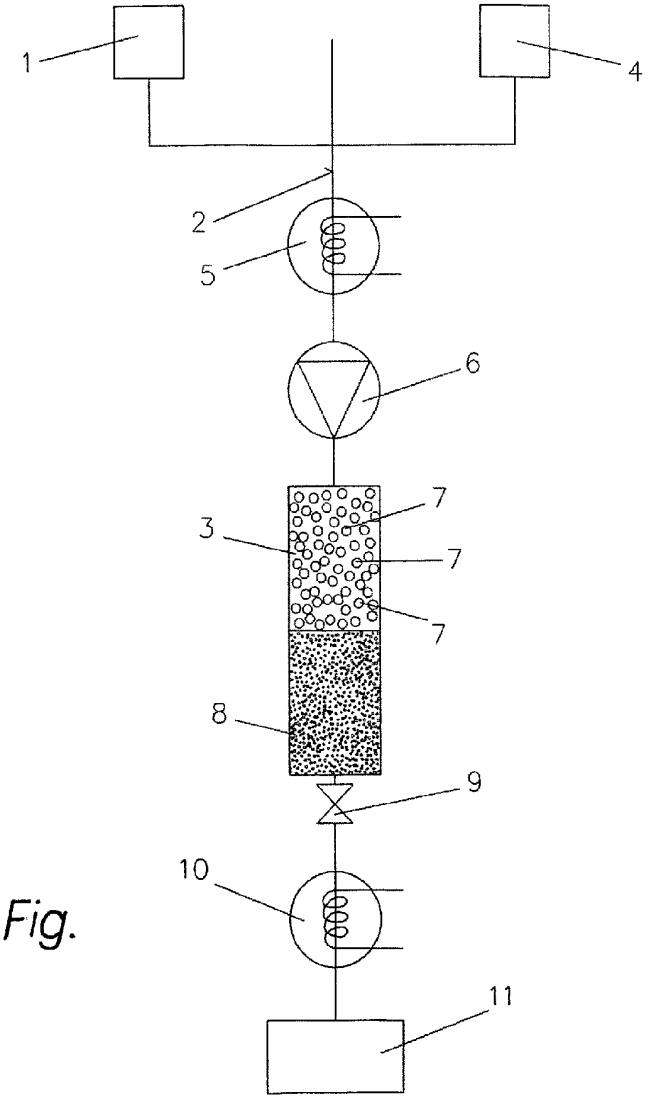

Fig.