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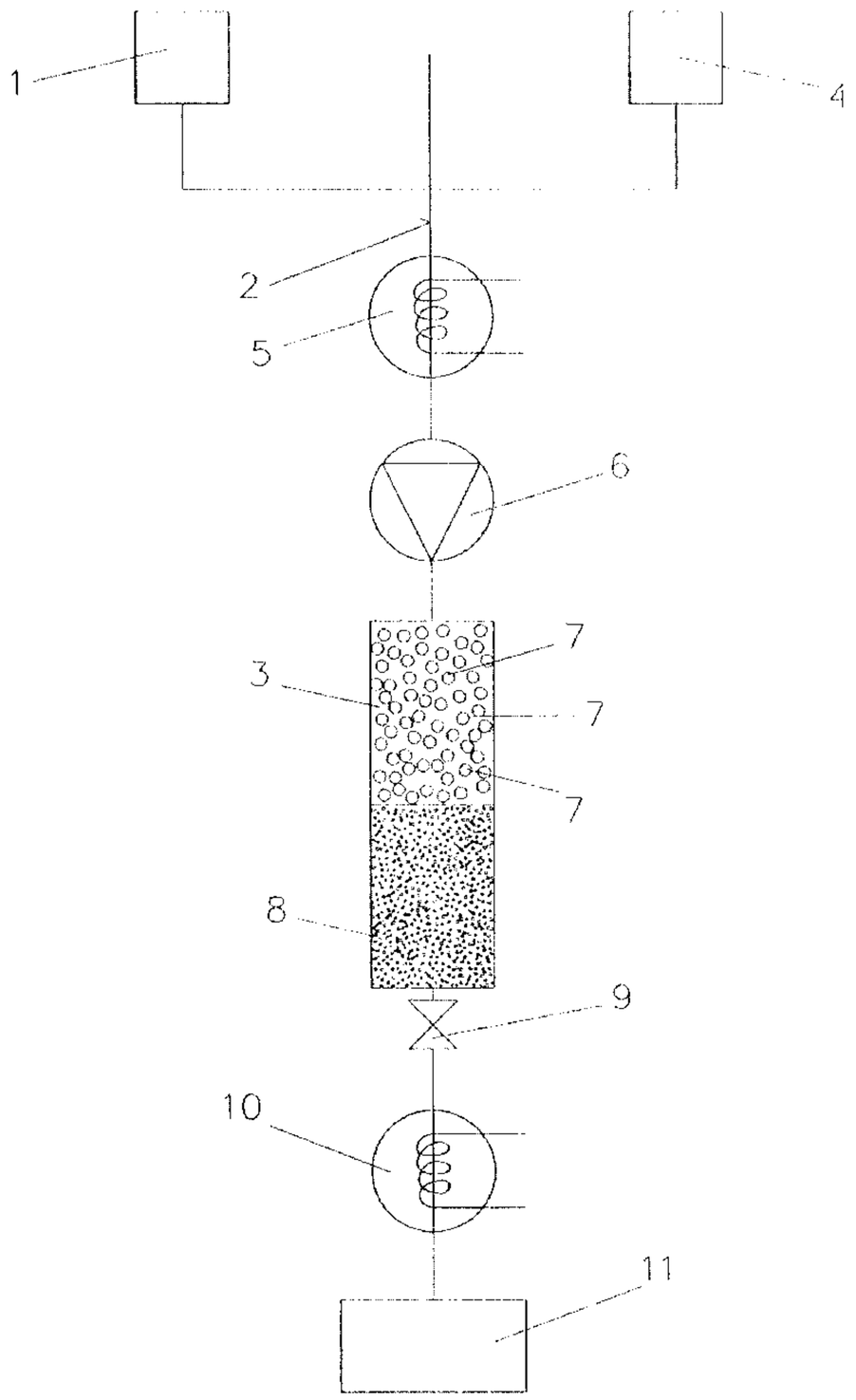
(54) Titre : PROCEDE ET INSTALLATION D'ESTERIFICATION D'ACIDES GRAS
(54) Title: METHOD AND SYSTEM FOR THE ESTERIFICATION OF FATTY ACIDS



(57) Abrégé/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

(21) 2 480 901

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(57) Abrégé(suite)/Abstract(continued):
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.

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.

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 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 the 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 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.

Furthermore, a method and a device for the production of carboxylic acid ester are known from WO 90/08127 A, whereby the esterification is carried out in a counterflow reaction column. The carboxylic acid to be esterified is introduced into said counterflow reaction column from above and alcohol, in particular methanol, is introduced from below in vapour form. The mixture is practically circulated for esterification. Several plates with ion exchangers are arranged in the column, the carboxylic acid reacts with the alcohol in the esterification zones. The water which is produced during esterification is removed with the methanol vapour during the esterification process at the upper end of the column, while the ester is removed at the lower end of the column.

Moreover, a method for the catalytic or non-catalytic esterification of acids is known from US 5 324 853 A. In the course of said method the reaction mixture is heated in a container with several stirring devices, so that the water that is produced is removed in vapour form during the esterification process.

In US 5 945 529 A a transesterification process based on the counterflow principle and using an inert gas is described. In said method, the lower alcohol that is produced during the transesterification is removed by a strip gas during the process. The transesterification is carried out by means of a multistage column or a multistage counterflow reactor.

An esterification of unsaturated carboxylic acids is known from EP 0 713 857 A1. Here, the water, produced by the esterification, is extracted from the various esterification zones containing ion exchangers during the process with the help of a medium in vapour form. During the process the vapours are withdrawn and the reaction water is removed from the cycle. The reaction vessel that is used for such purpose has a fixed bed with 1 to 10 stages. Each stage is comprised of a filter- and catalyst bed. From the citation index of the WPI database, section Ch, week 199818, XP 00251804 a horizontal tank with stirring devices is known, wherein vapour is withdrawn during the process in order to extract water that is produced.

In conclusion, the WO 02/38529 A is referred to. In this publication, a method for the production of fatty acid esters of lower alcohols is described, wherein by means of neutralisation of the glycerine phase and by means of a subsequent esterification with an acid a diesel substitute fuel is produced.

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 pressure, whereby 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, and the pressure is reduced during the esterification, whereby the pressure loss maintains a high interphase, and in that said reaction is carried out in the reaction section at a temperature of 50 to 300 °C, in particular at 80 to 150 °C.

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 or powerful dynamic turbulence, 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.

Another advantage lies in the fact that the methanol remains liquid due to the high pressure. Furthermore, the high reaction rate is advantageously achieved as a consequence of the high temperature.

According to an embodiment of the invention, the high shear forces or powerful dynamic turbulence are produced by mechanical devices in the reaction section. 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. The integration of 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 by means of said 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, whereby a pump, in particular a high-pressure pump, is provided for the introduction of the liquid into the reaction section. The advantageous turbulence is created primarily by the rapid flow of the mixture around the balls or devices. The integration of a high-pressure pump has proven to be advantageous because the turbulence achieves high dynamics and thus a large interphase for the transesterification.

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 the transesterification can therewith 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.

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.

From the container 4, the lower alcohol, in particular methanol, is pumped together with the acid, in particular sulphuric acid, into the supply line 2 leading to the reaction section 3.

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 and the powerful dynamic turbulence respectively 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, however, 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, a strong-acid ion exchanger, in particular an ion exchanger resin, is provided 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.

KR/19/8/04

NEW PATENT CLAIMS

1.A method for the esterification of fatty acids and/or fatty acids contained in fats and oils with low monovalent alcohols with 1 to 4 carbon atoms, 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, characterised in that in a reaction section (3) the interphases of the mixture are enlarged by high or powerful dynamic shear forces and/or turbulence, whereby the esterification starts under pressure, whereby at the beginning of the reaction section (3) the pressure lies at 2 to 500 bar, in particular at 50 to 200 bar and most preferably between 70 and 150 bar and the pressure is reduced during the esterification, whereby the pressure loss maintains a high interphase, and in that said reaction is carried out in the reaction section (3) at a temperature of 50 to 300 °C, in particular at 80 to 150 °C.

2.A method according to claim 1, characterised in that the high shearing forces and the powerful dynamic turbulence respectively are produced by mechanical devices in the reaction section (3).

3.A method according to claim 1 or 2, characterised in that the large interphases are created by ultrasound.

4.A method according to at least one of the claims 1 to 3, characterised in that the reaction section (3) is followed by a non-turbulent post-reaction section (8).

5.A method according to at least on e of the claims 1 to 4, characterised in that in the post-reaction section (8) a

pressure, preferably the initial pressure of the reaction section (3), is maintained or possibly further reduced.

6. A method according to at least one of the claims 1 to 5, characterised in that the post-reaction section (8) is filled with strong-acid ion exchangers

7. A system for the implementation of the method according to at least one of the claims 1 to 6, characterised in that the reaction section (3) is a pipe filled with balls (7) of the same size or different sizes and/or possibly has devices such as baffles, propellers and the like, whereby a pump, in particular a high-pressure pump (6), is provided for the introduction of the liquid into the reaction section (3).

8. A method according to claim 7, characterised in that an ultrasound device is provided in the reaction section (3).

9. A system according to claim 7 or 8, characterised in that the reaction section (3) is preceded by a heater (5) and in that the reaction section (3) or the post-reaction section (8) is possibly followed by a cooler (10).

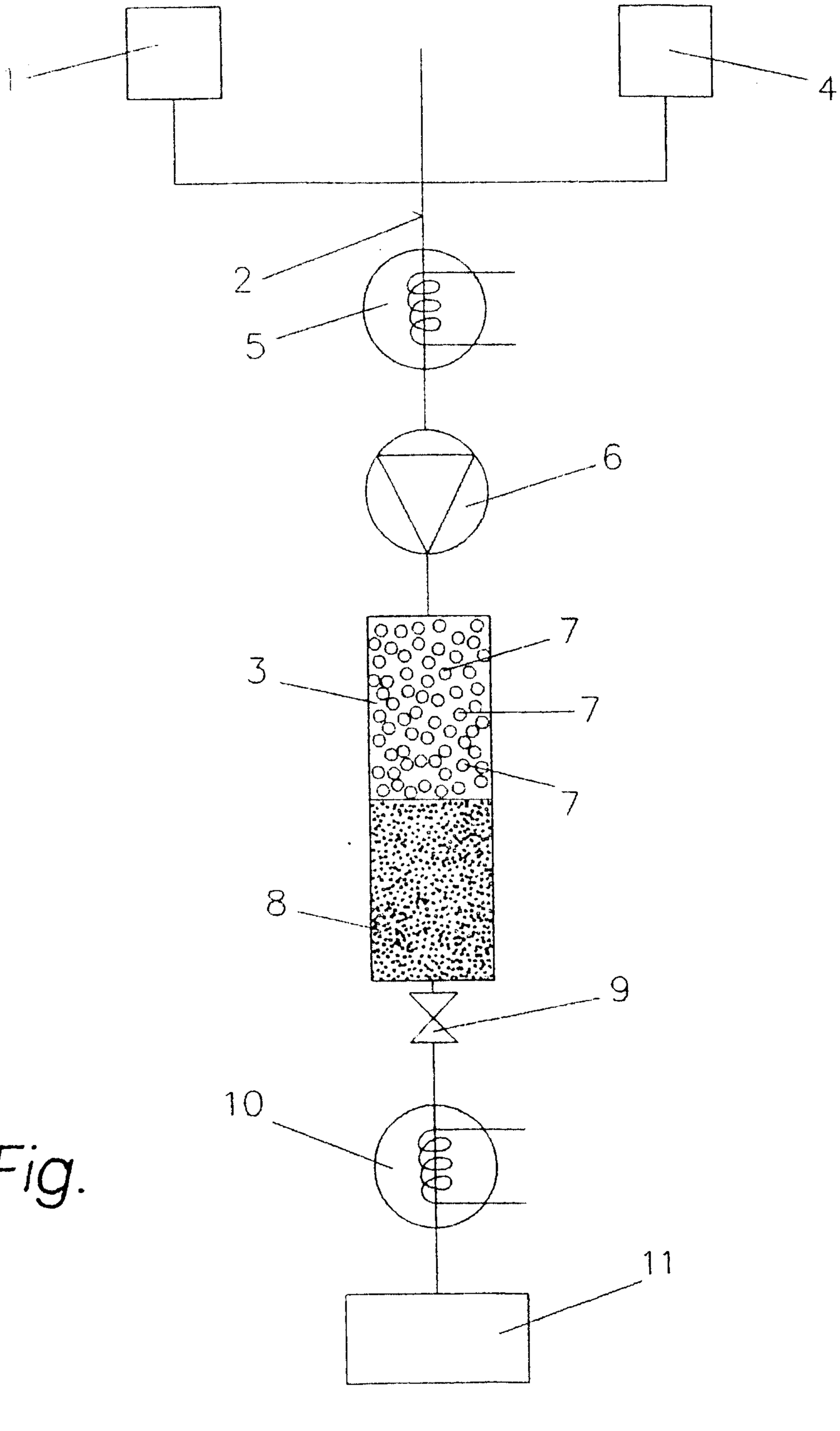
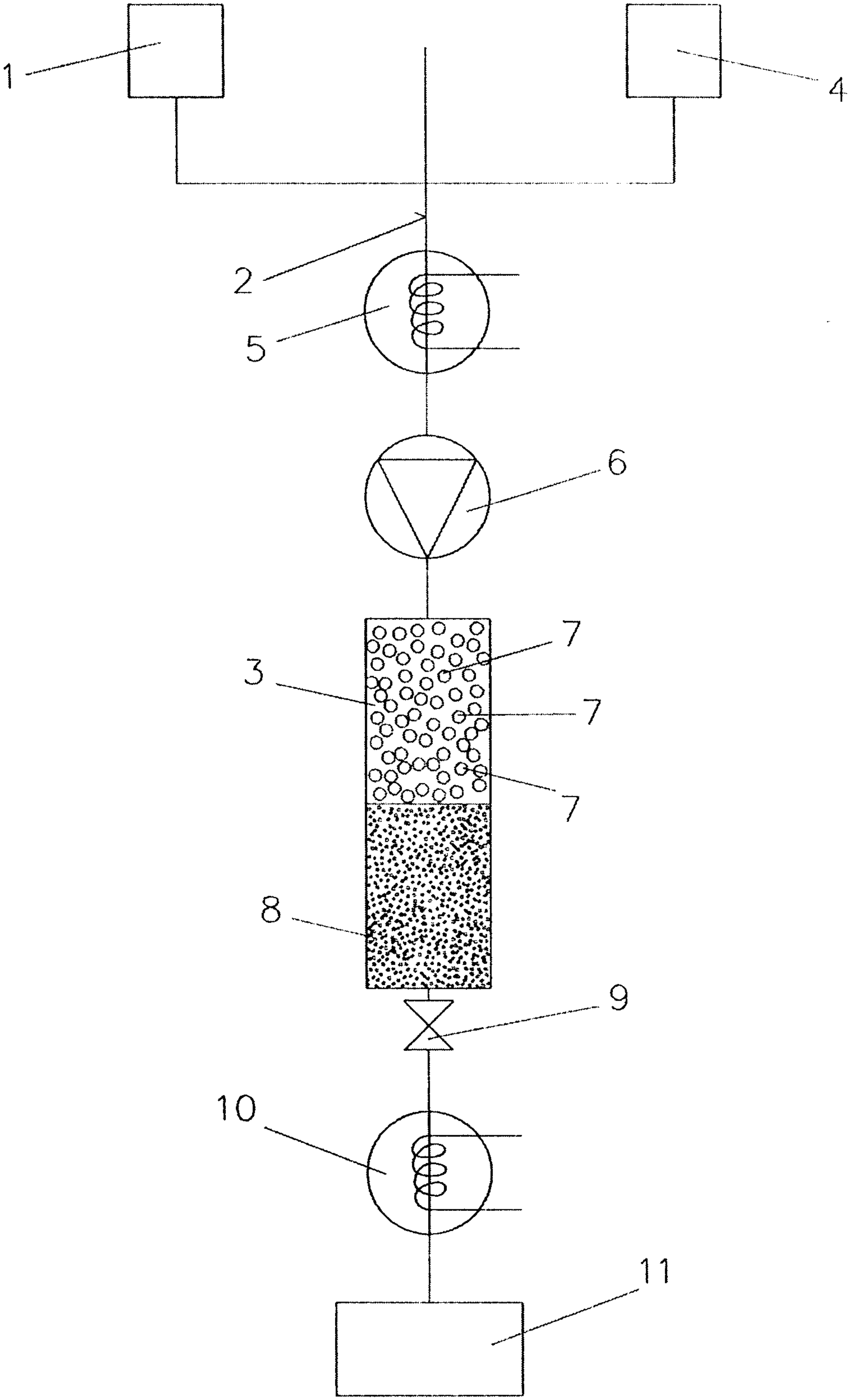


Fig.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